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MATHEMATICS

ON THE THEORY OF REGULAR PERTURBATIONS

By I. M. LIFSHITZ

(Communicated by S. L. Soboleff, Member of the Academy, 29.III.1945)

1. A number of physical problems can be reduced to the problem of the perturbation theory formulated as follows. Given the spectral resolution of the Hermitian operator L (undisturbed operator), investigate the spectral resolution of the sum of operators $L+t\Lambda$, where Λ is the Hermitian operator of perturbation, and t is an arbitrary real parameter.

The theory of small perturbations gives the solution of this problem, but only if the smallness of the operator $t\Lambda$ is postulated by a special assumption (see below). However, considerable interest may often attach to cases where $t\Lambda$ is not assumed to be necessarily small. Hereafter is built up a perturbation theory requiring no smallness of $t\Lambda$. Further on, this theory is applied to certain important classes of perturbations, especially to perturbations in a quasi-continuous spectrum and to local perturbations.

2. Let L be a semi-bounded Hermitian operator with a discrete spectrum: λ_p, its eigenvalue; Ψ_p, the corresponding normed eigenfunctions. The perturbation caused by the Hermitian operator Λ is said to be regular if the expression

$$\mathrm{Sp}\,\{(L-z)^{-1}\Lambda\}^{2n} < \infty \tag{1}$$

converges for some integer n (z is an arbitrary number different from λ_p). This condition implies a sufficiently rapid decrease of the quantities $\Lambda_{pq}/\sqrt{\lambda_p\lambda_q}$; $\Lambda_{pq}=(\Lambda\Psi_p\,\Psi_q)$.

We will now consider the important case, where the condition (1) is fulfilled for $n=1$

$$\sum_{p,\,q}\frac{|\Lambda_{pq}|^2}{|\lambda_p\lambda_q|} < \infty \tag{2}$$

Denote by μ_p an arbitrary sequence of real numbers, satisfying the condition

$$\sum_{r}\frac{|\Lambda^*_{rr}|}{|\lambda^*_r-z|} < \infty \tag{3}$$

$$\Lambda^*_{pq}=\Lambda_{pq}-\delta_{pq}\mu_p;\ \lambda^*_p=\lambda_p+t\mu_p \tag{4}$$

The numbers λ^*_p are supposed to be all distinct.

With this the eigenvalues z_p of the disturbed operator $L+t\Lambda$, not coinciding with the numbers λ_p^*, are roots of the equation

$$1+t\sum_p \frac{c_p^*}{\lambda_p^*-z}=0 \tag{I}$$

$$c_p^*=\Lambda^*(p)+\ldots+\frac{t^n}{n!}\sum_{p_1\ldots p_n}\frac{\Lambda^*(pp_1\ldots p_n)}{(\lambda_{p_1}^*-\lambda_p^*)\ldots(\lambda_{p_n}^*-\lambda_p^*)}+\ldots$$

$$\Lambda^*(p_1\ldots p_n)=\begin{vmatrix}\Lambda_{p_1p_1}^*\ldots\Lambda_{p_1p_n}^*\\ \cdots\cdots\cdots\\ \Lambda_{p_np_1}^*\ldots\Lambda_{p_np_n}^*\end{vmatrix}$$

The eigenfunctions φ_p corresponding to z_p are given (up to the norm) by the converging expression

$$\varphi_p=t\sum_q\frac{b_{pq}^*\psi_q}{\lambda_q^*-z_p} \tag{II}$$

$$b_{pq}^*=\Lambda\binom{q}{p}+\ldots+\frac{t^n}{n!}\sum_{p_1\ldots p_n}\frac{\Lambda^*\binom{qp_1\ldots p_n}{pp_1\ldots p_n}}{(\lambda_{p_1}^*-z_p)\ldots(\lambda_{p_n}^*-z_p)}$$

$$\Lambda^*\binom{q_1\ldots q_n}{p_1\ldots p_n}=\begin{vmatrix}\Lambda_{p_1q_1}^*\ldots\Lambda_{p_1q_n}^*\\ \cdots\cdots\cdots\\ \Lambda_{p_nq_1}\ldots\Lambda_{p_nq_n}\end{vmatrix}$$

Let us dwell in brief upon how (I) is obtained. Construct the operator M with a system of eigenfunctions ψ_p and with numbers μ_p for its eigenvalues. If the number z_p coincides with none of the numbers $\lambda_p^*=\lambda_p+t\mu_p$, the equation from which the eigenfunctions φ_p of the disturbed operator can be determined

$$(L-z_p+t\Lambda)\,\varphi_p=0 \tag{5}$$

(z_p is the eigenvalue of $L+t\Lambda$) is equivalent to the equation

$$\varphi_p+tK_{z_p}\varphi_p=0;\quad K_z=(K+LM-z)^{-1}(\Lambda-M) \tag{6}$$

or, in the representation ψ_p (in which L and M have diagonal form)

$$a_r+t\sum_q\frac{a_q\Lambda_{qr}^*}{\lambda_r^*-z}=0;\ a_r=(\varphi,\psi_r);\quad \varphi=\sum_r a_r\psi_r \tag{7}$$

(for brevity, z and φ are written without the subscript p). The conditions (2) and (3) render the sum

$$\sum\frac{|\Lambda_{pq}^*|^2}{|\lambda_p^*-z|\,|\lambda_q^*-z|}<\infty \tag{8}$$

convergent. In virtue of (7) and owing to (3) and (8) the eigenvalues of z_p, not coinciding with the numbers λ_p^*, are zero values of the function $\Phi(z)$ which represents a converging determinant

$$\Phi(z)\equiv D(1+tK_z)=1+tK_1(z)+\ldots+\frac{t^n}{n!}K_n(z)+\ldots \tag{9}$$

$$K_n(z)=\sum_{p_1\ldots p_n}\frac{\Lambda^*(p_1\ldots p_n)}{(\lambda_{p_1}^*-z)\ldots(\lambda_{p_n}^*-z)} \tag{10}$$

Developing the meromorphic function $\Phi(z)$ with respect to the poles (the λ_p^* are taken to be distinct) we get (I).

It may be remarked that if $n > 1$ in (1), one has to proceed not from equation (6) but from its $2n$th iteration.

Until now the sequence μ_r (and accordingly, $\lambda_r^* = \lambda_r + t\mu_r$) has been subject to no restriction, except the condition (3). This condition it satisfied automatically as soon as it is assumed that $\mu_r = \lambda_{rr}$, whereby the formulae (I) and (4) yield:

$$1 + t \sum \frac{c_p^*}{\lambda_p + t\Lambda_{pp} - z} = 0; \quad \lambda_p^* = \lambda_p + t\Lambda_{pp}; \quad \Lambda_{pq}^* = \Lambda_{pq} - \delta_{pq}\Lambda_{pp} \qquad \text{(Ia)}$$

This choice of the sequence μ_r is not, of course, the only possible one. If, for instance, $\sum_p |\Lambda_{pp}/\lambda_p| < \infty$, we may put $\mu_p = 0$, $1 + t \sum_p \frac{c_p}{\lambda_p - z} = 0$. If some of the numbers λ_q^* degenerate, terms with higher powers of the respective expressions of $1/(\lambda_q^* - z)$ will appear in the expansion (I). If necessary, the degeneration can be avoided by changing the values of μ_r.

3. The representation of eigenvalues as roots of the meromorphic function $\Phi(z)$ developed with respect to its poles permits some conclusions to be made regarding the oscillation properties of the eigenvalues of the disturbed operator. Some of them may be noted here.

Let the numbers λ_p^* be arranged in an increasing order. It can then be stated that:

a) If two consecutive coefficients c_p^* and c_{p+1}^* are of the same sign, then at least one eigenvalue of z_q of the disturbed operator lies between the numbers λ_p^* and λ_{p+1}^*.

b) If the coefficients c_p^* are all of the same sign, the numbers λ_p^* and z_p interlace.

The property b) can be generalized as follows. The sequences α_p and β_p are said to have an interlacement of order k, if it is possible to build $k-1$ interlacing sequences $\mu_p^{(1)}, \ldots, \mu_p^{(k-1)}$ such that $\mu_p^{(1)}$ is interlaced with α_p, and $\mu_p^{(k-1)}$ is interlaced with β_p (an instance of the interlacement of this kind is furnished by the sequence of zeros of a function and the sequence of zeros of its kth derivative). Now the following property may be established:

c) If the sequence c_p^* (arranged in an increasing order of λ_p^*) changes sign k times, then the sequences λ_p^* and z_p have an interlacement of order k.

These properties permit the problem to be analysed quantitatively, as well as qualitatively for a wide class of perturbations.

4 If the parameter t is small enough, then putting in (I) and (II)

$$z_p = \lambda_p + t\lambda_p^{(1)} + \cdots; \quad \varphi_p = \psi_p + t\psi_p^{(1)} + \cdots \qquad (11)$$

we obtain the ordinary formulae of the theory of small perturbations:

$$\lambda_p^{(1)} = \Lambda_{pp}; \quad \psi_p^{(1)} = \sum_{q \neq p} \frac{\Lambda_{pq}}{\lambda_p - \lambda_q} \psi_p \qquad (12)$$

However, the principal value of the method is that it can be applied expressly to those classes of perturbations in which t is not assumed to be small, and also to cases where the expansions (11) are not valid for small t. The latter circumstance takes place near the boundary of the continuous spectrum whenever the undisturbed operator has such spectrum. The method proposed here admits of an extension to this case also.

Physical-Technical Institute.
Academy of Sciences of the Ukrainian SSR.
Kharkov.

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MATHEMATICS

ON THE EXISTENCE OF THE TOTAL DIFFERENTIAL ON THE BOUNDARY OF A PLANE DOMAIN

By A. MYSHKIS

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I. By a domain G with the boundary $\tilde{G}$ is to be understood any open plane set. A function $f(B)$ defined on G in a neighbourhood of $A \in \overline{G}$ is said to possess the total differential $dz = a\,dx + b\,dy$ (and the surface $z = f(B)$ to possess a tangent plane) at A if $\lim\limits_{B \to A} f(B) = f(A)$ is in existence, and $f(B) - f(A) = a(x_B - x_A) + b(y_B - y_A) + O(|x_B - x_A| + |y_B - y_A|)$ $(B \in G)$.

The total differential (provided it exists) is not determined uniquely if and only if the set G has a tangent l_A at A (*i. e.* there exists a straight line l_A passing through A such that for every pair of angles with vertices at A enclosing l_A, the part of G belonging to a sufficiently small neighbourhood of A lies within these angles). In case there is such a straight line l_A, the tangent planes at A (provided that at least one tangent plane is in existence) form the cluster of planes with the axis projecting in l_A, with the exception of the vertical plane. Contrary to what takes place for $A \in G$ in the case where $A \in \tilde{G}$, the existence of the total differential of a continuous (at A) function $f(B)$ does not follow from the existence of the limits of the continuous (in G) derivatives f'_x, f'_y at A. It is possible to construct a domain G bounded by a simple (*i.* e. without self-intersections) closed rectifiable curve $\tilde{G}$ and a function $f(B)$, which is continuous on $\tilde{G}$ and has uniformly (in $\bar{G}$) continuous derivatives f'_x and f'_y, but has no total differential at a certain point $A \in \tilde{G}$.

Following Lavrentieff's notation [1], we denote by $d_r(B_1B_2)$ $(B_1 \in G, B_2 \in G)$ the greatest lower bound of lengths of rectifiable curves in G joining B_1 with B_2, provided such curves exist; otherwise, we put $d_r(B_1B_2) = \infty$. If $A \in \tilde{G}$, $B \in G$, we define: $d_r(AB) = \liminf\limits_{B_1 \to A, B \in G} d_r(BB_1)$. By $r(AB)$ we mean the distance from A to B. A point $A \in \tilde{G}$ will be called well accessible if $d_r(BA)/r(BA)$ $(B \in G)$ is bounded in a neighbourhood of A. Otherwise A will be called badly accessible point.

Theorem. *Let $f(B)$ be a function defined on G near a well accessible point $A \in G$. Suppose there exists* $\lim\limits_{B_1 \to A, B \in G} f(B) = f(A)$, *and all four derived numbers $D_x f$ (resp. $D_y f$) have the limit a (resp. b) at A. Then $adx + bdy$ is the total differential of f at A, which is called limit total differential in this case. Conversely, if $\overline{A} \in \tilde{G}$ is a badly accessible point, then there is a function f on G such that* $\lim\limits_{B \to A, B \in G} f(B) = 0$. *$D_x f$ and $D_y f$ are bounded in G and tend to 0 as $B \to A$, but f has no total differential at A.*

Proof. Suppose that $d_r(BA)/r(BA) < C$ and $|D_x f - a| + |D_y f - b| < \varepsilon$ for $r(AB) < 2CR$. Let $r(BA) = r < R$. Choose the points $B_0 = B, B_1, \ldots, B_i, \ldots$, so as to have $B_i \in G$, $d_r(B_i B_{i+1}) < C_r/2^i$, $r(AB_i) \leqslant r/2^i$ $(i = 0, 1, \ldots)$. We join B_i with B_{i+1} by a line in G of length $(< C_r/2^i)\sqrt{2}$ consisting of a finite number of straight line segments which are alternately parallel to the coordinate axes. Estimating the increments of the function on these segments, we have $|f(B_i) - f(B_{i+1}) - a(x_{B_i} - x_{B_{i+1}}) - b(y_{B_i} - y_{B_{i+1}})| < Cr(\sqrt{2}/2^i)\varepsilon$ $(i = 0, 1, \ldots)$. Now we sum all these inequalities and obtain

$$|f(B) - f(A) - a(x_B - x_A) - b(y_B - y_A)| < 2\sqrt{2}Cr\varepsilon$$

as was to be proved.

Conversely, suppose $d_r(AB)$ does not tend to 0 as $B \to A$, $B \in G$. Choose $B_0, B_1, \ldots B_i, \ldots (B_i \in G)$ so as to have $d_r(AB_i) > \varepsilon$, $d_r(B_i B_j) > \varepsilon$ $(i, j = 0, 1, \ldots; i \neq j)$, $\sum_0^\infty r(AB_i) < \infty$; suppose also that the sequence of rays AB_i is convergent. Put $f_i(B) = r(AB_i)[\varepsilon - d_r(BB_i)]$ $(B \in G, d_r(BB_i) \leqslant \varepsilon)$ and $f_i(B) = 0$ $(B \in G)$, $d_r(BB_i) > \varepsilon)$. Then $f(B) = \sum_0^\infty (-1)^i f_i(B)$ is the function required. In particular, $f(B_i) - f(A)/r(AB_i) = (-1)^i \varepsilon$, as was to be proved.

Suppose now that $d_r(AB) \to 0$ as $B \to A$ $(B \in G)$, but $\limsup_{B \to A,\, B \in G} \frac{d_r(AB)}{r(AB)} < \infty$. Put $\psi(r) = \sup_{r(AB) = r, B \in G} d_r(AB)$. Then $\psi_r \to 0$ as $r \to 0$ and $\limsup_{r \to 0} \frac{\psi(r)}{r} = \infty$. We choose $\varphi(x)$, $x > 0$, under the conditions: $\varphi(x) \to 0$ as $x \to 0$, all $D_x \varphi \to 0$ as $x \to 0$, and $\limsup_{r \to 0} \frac{\varphi[\psi(r)]}{r} = \infty$. Then $\varphi[d_r(AB)]$ is the function required.

Note that the theorem holds for Euclidean spaces of any dimension.

The space formed by revolution of the curve mapping the Cantor set E onto a segment round the centre of E gives an example of a function, which is uniformly continuous on the sum of contiguous rings G and possesses the derivatives equal to 0 on G, but has no total differential at any point of $\tilde{G}$. There are simply connected domains the boundaries of which consist of badly accessible points only.

In case there exist limits of continuous (in G) derivatives of f at A, but the limit total differential does not exist at A, the non-limit total differential of f at A may still exist. There is an example of a simply connected domain G and a function f uniformly continuous, together with its derivatives f'_x, f'_y, on G such that the total differential exists and is unique at every point of $\tilde{G}$, but it is non-limited differential at the points that form a closed curve. On the other hand, we have an example of locally connected domain G with a badly accessible point $A \in G$ such that the existence of the limits

$$\lim_{B \to A, B \in G} D_x f = a, \quad \lim_{B \to A, B \in G} D_y f = b$$

and of the total differential $a_1 dx + b_1 dy$ at A implies $a = a_1$, $b = b_1$. The question is open by what condition the property of good accessibility must be replaced if f is supposed to be uniformly continuous in a neighbourhood of $A \in G$.

II. Such a distinction of differential properties near the boundary points is applicable to a problem suggested by I. Petrovsky. Suppose G, G_1 and G_2

to be open, $G = G_1 + G_2 + D$, $G_1 \cap G_2 = G_1 \cap D = G_2 \cap D = 0, G \cap G_1 = G \cap \tilde{G}_2 = D$. Let f_1 be continuous on $G\bar{G}_1$ while f_2 is continuous on $G\bar{G}_2$, and $f_1 = f_2$ on D. Suppose f_1 and f_2 to have continuous derivatives on G_1 and G_2, respectively. Assume also $|f'_{1x} = f'_{2x}| + |f'_{1y} = f'_{2y}| > 0$. The question is, under what conditions D has a simple structure, for instance, is a curve $x = x(t)$, $y = y(t)$ with continuous $x'(t)$, $y'(t)$ and $|x'(t)| + |y'(t)| > 0$.

If we assume only the existence on D of distinct limits of the total differentials of f_1 and f_2 taken on G_1 and G_2, the structure of D may be still very complicated. If we assume the existence at a point $A \in D$ of distinct tangent planes to $z = f_1$ and $z = f_2$, then D has a tangent at A, which is the projection of the intersection of both tangent planes. If the differentials depend continuously on the point of D, then the direction of the tangent to D varies continuously; this takes place, for instance, in case the differentials are limit differentials. In this case the elementary singularities are return points. More complicated singularities can be constructed from these simple ones. If we assume the existence and the uniqueness of distinct total differentials on D, then the return points are excluded, though other singularities may still occur.

Suppose D has the equation $y = \varphi(x)$, $a < x < b$, where φ is single-valued and continuous. Then if there are distinct total differentials of f_1 anf f_2 on D, $\varphi(x)$ possesses the derivative $\varphi'(x)$ (which may be infinite, but of definite sign) everywhere, except possibly an at most enumerable set of return points ([3]). If the uniqueness of these differentials is assumed, then $\varphi'(x)$ exists everywhere. If we assume only the existence on D of the limits of the total differentials, then such domains D may occur as do not have a tangent everywhere.

Consider, in general, a set D defined in a plane domain G, dense in itself and closed with respect to G, and having a tangent l_A at everyone of its points; the direction of l_A is supposed to depend continuously on D. Let also the following condition be fulfilled: for every point $A \in D$ every neighbourhood $U(A)$ contains points of D lying on both sides of the normal n_A to D. This is realized, for instance, in Petrovsky's problem under the condition of uniqueness of the total differentials of f_1 and f_2 on D. One can investigate the structure of D under the more restrictive conditions. Under our final assumption that every compact subset of G overlaps only with a finite number of connectivity components of $G - D$, the set D has the following structure near everyone of its points: suppose $A = (0, 0)$ and l_A coincides with the x-axis; then D consists, in a neighbourhood of A, of a finite number of parts $y_i(x)$ $(i = 1, 2, \ldots, n)$ with continuous derivatives defined on the segments $[-\varepsilon, 0]$ and $[0, \varepsilon]$ $[\varepsilon = \varepsilon(A)]$; $y_i(0) = y'_i(0) = 0$ $(i = 1, 2, \ldots, n)$; any two curves have a unique common point A. If $n > 2$, then A is called branch point of D with the index $n - 2$. Thereby $D = D_1 + D_2 + \ldots$, where every D_i is a curve $x = x(t)$, $y = y(t)$ with continuous $x'(t)$, $y'(t)$, $|x'(t)| + |y'(t)| > 0$, having no multiple points, except possibly their end-points of one of the following types:

1) $0 \leqslant t \leqslant 1$; $x(0) = x(1)$; $y(0) = y(1)$; $x'(0) = x'(1)$; $y'(0) = y'(1)$;

$$D_i \cap \sum_1^{i-1} D_k = 0;$$

2) $0 \leqslant t \leqslant 1$; $x(0) = x(1)$; $y(0) = y(1)$; $x'(0) = x'(1)$; $y'(0) = y'(1)$,

$$D_i \cap \sum_1^{i-1} D_k = A_i\{x(0), y(0)\};\ D_i \text{ touches } \sum_1^{i-1} D_k \text{ at } A_i;$$

3) $0 \leqslant t \leqslant 1$; $|x(0)-x(1)|+|y(0)-y(1)|>0$; $D_i \cap \sum_1^{i-1} D_k = B_i^1\{x(0), y(0)\} + B_i^2\{x(1), y(1)\}$, where D_i touches $\sum_1^{i-1} D_k$ at B_i^1 and B_i^2;

4) $0 \leqslant t \leqslant \infty$; $D_i \cap \sum_1^{i-1} D_k = C_i\{x(0), y(0)\}$; D_i touches $\sum_1^{i-1} D_k$ at C_1 and the distance from the point $\{x(t), y(t)\}$ to G tends to 0 as $t \to \infty$ (or $x^2(t)+y^2(t) \to \infty$);

5) $-\infty < t < +\infty$; $D_i \cap \sum_1^{i-1} D_k = 0$ and the same limit relations hold for $|t| \to \infty$ as in the case 4).

Thereby the intersection of D with any compact subset of G is exhausted by a finite number of such operations. Conversely, any such process generates a set D possessing the above properties. In case G is connected and r-connected and $G-D$ consists of (a finite number) k_{G-D} connectivity components, then the whole D is exhausted by a finite number of these operations; in this case we have, provided G is bounded:

$$k_{D+\tilde{G}} + \frac{\sum p_i}{2} + \frac{p}{2} = r - 1 + k_{G-D}$$

where $k_{D+\tilde{G}}$ is the number of connectivity components of $D+\tilde{G}$; $\sum p_i$ is the sum of indices of all the branch points of D; p is the number of branches going to $\tilde{G}$. The above formula enables us to find all possible configurations of D with respect to G. For instance, if $r=1$, $k_{G-D}=2$, we have four possible cases: a circle, a straight line, a ρ-shaped figure and a figure like a tennis racket; the last two cases are topologically equivalent. In particular, in Petrovsky's problem, D may be either a circle or a straight line (or, putting it more accurately, of form 1) or 5), provided G, G_1 and G_2 are connected and there exist distinct unique and continuous total differentials for f_1, f_2 on D. When $r=1$, $k_{G-D}=3$, there are 154 possible configurations of D with respect to G, and 19 of them are topologically different.

III. Such a detailed distinction can be also carried through in the theory of partial differential equations. For instance, considering boundary problems of the first order, the values of the derivatives on the boundary can be understood to mean either the coefficients of the existing total differential (which is natural only from the viewpoint of the theory of functions), or the partial derivatives, or, finally, the coefficients of the limit total differential. All these problems are non-equivalent.

The N. E. Joukovsky War-Aviation Academy.

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AERODYNAMICS

FUNDAMENTAL PROBLEMS OF FLUID DYNAMICS FOR BOUNDARY LAYER ON AIRPLANE WING

By A. M. FEINSILBER

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A new direction in the theory of the boundary layer was layed down by the theorem of kinetic energy established by Leibenson (²). This theorem was used by Golubev (³) for an arbitrary exponent. The method of aerodynamic integral invariants suggested in the present paper is an outgrowth of the ideas put forward by Leibenson and Golubev and their extension to the case of a compressible fluid.

The method is based on the construction of invariant equations which permit the two fundamental problems of the boundary layer theory to be treated separately; these problems are to find the law of velocity and density distribution in the layer, and to determine the thickness of the layer. The problem is put in the general way; that is, 1) for any Prandtl number, 2) for an arbitrary temperature gradient at the surface of the aerofoil, and 3) for a laminar as well as turbulent layer of a compressible or incompressible fluid.

Let us adopt the following notation: u and v, the velocity components in the layer; ρ, density; T, absolute temperature; p, pressure; μ, dynamic coefficient of viscosity; ν, kinematic coefficient of viscosity; k, Fourier coefficient of thermal conductivity; τ, stress due to viscosity; q, heat intensity; δ, the thickness of the layer; Re, Reynolds number; Pr, Prandtl number; Ba, Barstow number; $\varkappa$, adiabatic exponent. The values which these quantities take at the border of the layer are respectively denoted by $\bar{u}$, $\bar{T}$, and so on; the values at the wall, by T_0, μ_0, *etc.*

The differential equations of the boundary layer for a compressible fluid are

$$\rho u \frac{\partial u}{\partial x} - \int_0^y \frac{\partial (\rho u)}{\partial x} dy \frac{\partial u}{\partial y} = -\frac{dp}{dx} + \frac{\partial \tau}{\partial y} \tag{1}$$

$$c_p \left(\rho u \frac{\partial T}{\partial x} - \int_0^y \frac{\partial (\rho u)}{\partial x} dy \frac{\partial T}{\partial y} \right) = u \frac{dp}{dx} + \frac{\partial q}{\partial y} + \tau \frac{\partial u}{\partial y} \tag{2}$$

Our method rests on the two following theorems, which are described as the theorems of aerodynamic interval invariants.

Theorem 1 (on dynamic invariant). *Suppose we have the dimensionless variables* $t = y/\delta$; $\lambda = \bar{u}' \delta^2/\bar{\nu}$; $u_1 = u/\bar{u}$, $\rho_1 = \rho/\bar{\rho}$, *etc*; $\tau_1 = \delta\tau/\bar{\rho}\bar{u}$; $q_1 = \delta_q/\bar{k}\bar{T}$, *and*

the functions $P(\lambda)$ *and* $Q(\lambda)$ *defined by the formulae*

$$P(\lambda) = -\frac{\lambda}{2}\frac{d}{d\lambda}\ln\frac{\overline{u}'}{\overline{\mu\rho}\lambda}; \quad Q(\lambda) = \frac{d}{d\lambda}\ln\overline{u} \tag{3}$$

Let $F(u)$ *be a function of arbitrary form, subject only to the condition*

$$F(1) = 0 \tag{4}$$

Then equation (1) *together with the corresponding boundary conditions is equivalent to an infinite system of integral invariant equations:*

$$\frac{P(\lambda)\int_0^1 \rho_1 u_1 F dt + \lambda\frac{d}{d\lambda}\int_0^1 \rho_1 u_1 F dt - \lambda Q(\lambda)\int_0^1 [F'(u_1)(1-\rho_1 u_1^2) - \rho_1 u_1 F]\,dt}{\int_0^1 F'(u_1)\frac{\partial\tau_1}{\partial t}\,dt} = \text{invar}(F) \tag{5}$$

the boundary conditions remaining unaltered.

Theorem 2 (on thermodynamic invariant). *Let* $\Psi(T_1)$ *be a function of arbitrary form, subject only to the condition*

$$\Psi(1) = 0 \tag{6}$$

Then equation (2) *together with the boundary conditions is equivalent to the ystem of equations:*

$$\frac{[P(\lambda)+\lambda Q(\lambda)]\int_0^1 \rho_1 u_1 \Psi dt + \lambda\frac{d}{d\lambda}\int_0^1 \rho_1 u_1 \Psi dt - (x-1)\,\overline{\text{Ba}}^2 Q(\lambda)\int_0^1 \Psi'(T_1)\tau_1\frac{\partial u_1}{\partial t}\,dt}{\int_0^1 \Psi'(T_1)\frac{dq_1}{\partial t}\,dt} = \text{invar}(\Psi) \tag{7}$$

the boundary conditions remaining unaltered.

Proof of Theorems 1 and 2. Equations (1) and (2) are multiplied by $F'(u_1)$ and $\Psi'(T_1)$, respectively, and integrated with respect to y from 0 to δ. After a series of transformations such equations are obtained whose right-hand sides do not contain the arbitrary function F or Ψ, respectively. Accordingly, their left-hand sides must be invariant with respect to F or Ψ, respectively. The proof of the inverse statement presents no essential difficulties.

The infinite system of equations (5) and (7), which is obtained by varying the form of the functions F or Ψ, will just serve to find the laws of velocity and density distribution. The unknown functions u_1 and ρ_1 are sought for in the form of power series of λ:

$$\begin{aligned} u_1 &= a_0(t) + a_1(t)\lambda + \ldots \\ \rho_1 &= \frac{1}{T_1} = d_0(t) + d_1(t)\lambda + \ldots \end{aligned} \tag{8}$$

For determining the coefficients $a_i(t)$ and $d_l(t)$ we obtain a series of invariant relations which no longer contain the variable λ. Let us write down the first of them.

$$\frac{\int_0^1 F'[a_0(t)]\frac{d(\tau_1)_{\lambda=0}}{dt}}{\int_0^1 d_0(t)\,a_0(t)\,F[a_0(t)]\,dt} = \text{invar}(F) \tag{9}$$

From system (9) we find the unknown coefficients $a_i(t)$ and $d_l(t)$ in the form of polynomials of the k-th degree, where the value of k determines the accuracy of the solution.

Let us give some quantitative results.

For the boundary layer of a compressible fluid on a plate we find for the temperature distribution

$$T_1 = \frac{T_0}{T} + 0.911\left(1 + 0.558a - \frac{T_0}{T}\right)u_1 - \frac{a}{2}u_1^2 + 0.090\left(1 - 0.101a - \frac{T_0}{T}\right)u_1^2 \quad (10)$$

where $a = (\varkappa - 1)\,\mathrm{Pr}\overline{\mathrm{Ba}}^2$.

For the resistance law we find the expression

$$C_f = \frac{4A_0(a)}{\sqrt{T_0/T}}\sqrt{\frac{1}{\mathrm{Re}}} \quad (11)$$

where $A_0(a)$ is a known function.

The value of the Prandtl number affects the results considerably. For instance, for $\mathrm{Ba} = 2$ we have $A_0 = 0.064$ if $\mathrm{Pr} = 0.72$, and $A_0 = 0.049$ if $\mathrm{Pr} = 1$; the divergence is 24 per cent.

To put another example we can take a known velocity distribution in the boundary layer of a compressible fluid on an aerofoil of arbitrary form

$$u_1 = (1.62t - 0.86t^3 + 0.24t^4) + \lambda\,(0.357t - 0.500t^2 - 0.071t^3 + 0.214t^4) \quad (12)$$

The value $\lambda = -4.54$ corresponds to separation. The results obtained in computing the separation for circular and elliptic cylinders were in good agreement with the experiment.

For the turbulent layer of a compressible fluid we obtain the following relation between friction intensity, velocity and density:

$$\frac{\tau}{\tau_0} = \frac{\int_t^1 \frac{du_1}{dt}\int_0^t \rho_1 u_1\,dt\,dt}{\int_0^1 \rho_1 u_1(1-u_1)\,dt} \quad (13)$$

in the case of a plate and a similar, though a more complicated relation, in the case of an arbitrary aerofoil.

For an arbitrary aerofoil we obtain the following velocity distribution

$$\frac{u(1-\bar{u}_1)}{\sqrt{\tau_0/\rho}} = \frac{1}{\varkappa_1}\left[\sqrt{1+b(x)} - \sqrt{1+b(x)\,t} + \ln\frac{\sqrt{1+b(x)}-1}{\sqrt{1+b(x)\,t}-1}\right] \quad (14)$$

where $b(x) = 1 + \frac{\delta dp/dx}{\tau_0}$; $\varkappa_1$ is an experimental constant.

Comparisons with the results obtained experimentally by Gruschwitz [4], Kempf [5], Fage and Falkner [6] show the theory to be in good agreement with the experimental data.

The methods of the present work are also applicable to problems with axial symmetry.

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MATHEMATICAL PHYSICS

SOME THEOREMS OF THE THEORY OF ANISOTROPIC MEDIA

By B. HERMAN

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The symmetry of the anisotropy of some physical property, besides the symmetry of the structure of the medium, is closely connected with the rank of the tensor which defines it. In a medium which by way of approximation is taken to be continuous, the first thing to be considered are the rotating axes of symmetry*.

The following theorem is true for an arbitrary anisotropic medium.

If the medium has a rotating axis of symmetry C_N of order N, it is axially isotropic relative to this axis for all the physical properties defined by the tensors of the rank $r = 0, 1, 2, \ldots N-1$.

In other words, let the medium have a structural axis of symmetry C_N of order N. Then the components of the tensors of rank $r < N$ will be necessarily invariant, not only relative to the angle of rotation $\varphi = 2\pi/N$**, but also relative to rotation about this axis through an arbitrary angle $\varphi\,(0 \leqslant \varphi \leqslant 2\pi)$, which means that C_N for all the properties with $r < N$ is an axis of infinite order C_∞, or briefly $C_{N>r} \rightarrow C_\infty$.

The proof can be carried out as follows:

Let us introduce the circular unit vectors $\mathbf{j}_\alpha\,(\alpha = 0, 1, -1)$ related to usual Cartesian unit vectors $\mathbf{i}_1$, $\mathbf{i}_2$, $\mathbf{i}_3$ by the relations $\mathbf{j}_0 = \mathbf{i}_3$, $\mathbf{j}_1 = \frac{1}{\sqrt{2}}(\mathbf{i}_1 + i\mathbf{i}_2)$, $\mathbf{j}_{-1} = \frac{1}{\sqrt{2}}(\mathbf{i}_1 - i\mathbf{i}_2)$. The unit vectors $\mathbf{j}_\alpha$ are evidently connected with one another by the orthogonality relations

$$\mathbf{j}_{\alpha_1}\mathbf{j}_{\alpha_2} = \delta(\alpha_1 + \alpha_2)$$

where

$$\delta(\alpha_1 + \alpha_2) = \begin{cases} 1 \text{ if } \alpha_1 + \alpha_2 = 0 \\ 0 \text{ if } \alpha_1 + \alpha_2 \neq 0 \end{cases} \qquad \alpha_1, \alpha_2 = 0, 1, -1$$

Let $A_{\alpha_1\alpha_2\ldots\alpha_r}$ be a tensor of the rank r with 3^r components defined in $\mathbf{j}_\alpha$, where $\alpha_1, \alpha_2, \ldots \alpha_r$ take the values $0, 1, -1$. Evidently its components are

* On account of continuity the translation is left out of consideration. The existence of a centre of inversion C_i and a plane of symmetry σ can easily be taken into account. C_i does not influence the properties with odd r; σ converts to zero the components of the tensor containing the index of the axis σ an odd number of times.

** The latter is clear from the congruence of the operation C_N, and evidently takes place for all the physical properties of the medium with arbitrary r, without exception.

connected with the components of this tensor of the same rank r in the usual Cartesian coordinates.

By rotating about j_0, directed along the axis of rotation* C_N, through an angle φ the transformed components (marked with an accent) will be expressed through the initial ones in the following way:

$$\Lambda'_{a_1a_2\ldots a_r} = e^{i(a_1+a_2+\ldots+a_r)\varphi}\,\Lambda_{a_1a_2\ldots a_r} \quad -r \leqslant a_1+a_2+\ldots a_r \leqslant r \tag{1}$$

The presence of C_N gives, according to definition:

$$\Lambda'_{a_1a_2\ldots a_r} = \Lambda_{a_1a_2\ldots a_r} \text{ when } \varphi = 2\pi/N;$$

for $N < r$ it is possible only if

$$a_1 + a_2 + \ldots a_r = 0 \tag{2}$$

In this way only those components of the tensor $\Lambda_{i_1i_2\ldots i_r}$ can differ from zero (*i. e.* are consistent with the symmetry C_N, $N < r$), for which the sum of the indices satisfies the equation (2). However, as will be seen from equation (1), all these components are invariant relative to rotation through an arbitrary angle $\varphi\,(0 \leqslant \varphi \leqslant 2\pi)$, which proves the correctness of our theorem.

This result is quite clear from the physical point of view. Let us imagine that elements of the volume are cut off perpendicularly (or all at an equal angle) to the axis $C_{N>r}$ radially in different directions; then, according to the theorem just proved, all these elements of volume will be identical in all physical properties described by the tensors, the rank of which is $r = 0, 1, 2 \ldots, N-1$, respectively. So, when the medium has an axis $C_{N>r}$, it is at least axially isotropic in respect to all physical properties: scalar ($r = 0$), vectoral ($r = 1$), electric constant and heat conductivity (σ_{ik}), dielectric constant (ε_{ik}), susceptibility (χ_{ik}) and other ($r = 2$), piesoelectricity (λ_{ikl}), magnetostriction (Λ_{ikl}) ($r = 3$), tensor of the moduls or coefficients of elasticity (s_{iklm}), photoelasticity (tensor of the constants of optical tensions, ε_{iklm}) ($r = 4$), and other physical properties with $r < N$.

Because of $C_{N>r} \to C_\infty$, only those components of the tensor of rank $r < N$ will differ from zero, which are included in its linear invariant relative to rotation through an arbitrary angle about C_∞. They evidently represent in the system with the axis (3) $\| C_\infty$ a linear combination of tensors $\delta_{a_1a_2} = \begin{cases} 1, a_1 = a_2 \\ 0, a_1 \neq a_2 \end{cases}$ $(a_1, a_2 = 1, 2)$ with the corresponding tensor coefficients [which contain only the index (3)]. Thus, it is possible to write immediately the independent coefficient consistent with the symmetry $C_{N>r}$. For $r = 4$ (for instance, the tensor of the modulus or of the coefficients of elasticity $S_{i_1i_2i_3i_4}$) only the following components are different from zero (here $C_{N>4}$; the following equations are taken into consideration: $S_{i_1i_2i_3i_4} = S_{i_2i_1i_3i_4} = S_{i_2i_4i_1i_2} = S_{i_1i_3i_2i_4}$):

$$S_{3333},\ S_{3a_13a_2} = A_{33}\delta_{a_1a_2},\ S_{33a_1a_2} = B_{33}\delta_{a_1a_2},\ S_{a_1a_2a_3a_4} =$$
$$= A\delta_{a_1a_2}\delta_{a_3a_4} + B\,(\delta_{a_1a_2}\delta_{a_2a_4} + \delta_{a_2a_3}\delta_{a_1a_4})\ (a_1, a_2, a_3, a_4 = 1, 2)$$

The consideration of the general case is quite analogous. Different from zero for the arbitrary tensor $\Lambda_{i_1i_2\ldots i_3}$ of rank $r < N$ ($C_{r<N} = C_\infty \| (3)$) will be:

$$\underbrace{\Lambda_{33\ldots3}}_{r},\ \Lambda_{a_1a_2\underbrace{3\ldots3}_{r-2}} = \underbrace{A^P_{1\ldots3}}_{r-2}\delta_{a_1a_2},\ \Lambda_{a_1a_2a_3a_4\underbrace{3\ldots3}_{r-4}} = \sum_P \underbrace{A^P_{33\ldots3}}_{r-4}\ \delta_{a_1a_2}\delta_{a_3a_4}\ldots$$

and finally:

$$\Lambda_{a_1a_2\ldots a_r} = \sum_P A^P \delta_{a_1a_2}\ldots\delta_{a_{r-1}a_r}$$

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* The presence of an intersecting axis will be considered later; taking account of C_i and σ follows from the first note.

(or $\Lambda_{a_1 \ldots a_{r-1}}$ when r is an odd number). The tensor values invariant relative to rotation, like $A^{P}_{33\ldots3}$ and so on, are in general different for the transpositions $P\begin{pmatrix} 1 & 2 & \ldots & r \\ a_1 & a_3 & 3 & \ldots & 3 \end{pmatrix}$, which is considered by the index P above. The presence of the conditions of symmetry for the described physical property naturally decreases the number of the different values such as $A^{P}_{33\ldots3}$, as can be seen from the example with $r=4$ quoted in the text. The total number of components $\Lambda_{\underbrace{33\ldots3}_{k}\underbrace{a_{k+1}\ldots a_r}_{r-k}}$ containing the index (3) k times, is equal to $\binom{r}{k} 2^{r-k}\left(\sum \binom{r}{k} 2^{r-k} + 2^r = 3^r\right)$. The existence of a plane σ passing through C_∞ gives nothing new. $\sigma \perp C_\infty$ gives C_i.

It follows from (1) and (2) that the greatest simplification of the tensor of the rank r depending on the consistency with the symmetry C_N is obtained already for $N=r+1$. The further increase of the symmetry (increase of N) does not impose, as is evident from (1), complementary restrictions on the components of the tensor, and cannot therefore lead to further simplifications.

The symmetry of the anisotropy in the presence of two intersecting axes can be obtained by replacing, according to the well known Hamilton's theorem ([1, 2]), the result of two rotations round these axes by one rotation round a new axis. Let us prove the following theorem:

If the medium has two intersecting axes C_{N_1} and C_{N_2}, the order of one of them being $N_1 > r$, it is (with the exception of the case $C_{N_2=2} \perp C_{N_1>r}$) space isotropic relative to all the physical properties defined by the tensors with the rank $r=0,\ 1,\ 2,\ \ldots\ N-1$.

If $N_2 > r$, the proof follows from the fact that $C_{N_1>r}$ and $C_{N_2>r}$ are axes of infinite order. Therefore the rotation round C_{N_1} and C_{N_2} at arbitrary angles leaves invariant the components of the tensor of the rank $r\,(r < N_1, N_2)$, which defines the physical property, and therefore its components remain invariant also at every space rotation which can be obtained as resulting from these rotations; that means isotropy, according to definition.

The case $N_2 \leqslant r\,(N_1 > r)$ which means $C_{N_1>r} \rightarrow C_\infty$, $C_{N_2>r}$, leads (with the exception of $C_{N_2=2} \perp G_{N_1>r}$) to the same result. Indeed, according to the above considerations, for the proof of isotropy it is sufficient to show that by rotations through an arbitrary angle about $C_{N_1>r} \rightarrow C_\infty$ and through a multiple angle of $2\pi/N_2$ about C_{N_2}, it is possible to obtain at least one more axis of infinite order C'_∞. The angle ψ of the resulting rotation (see figure) lies in the interval

$$\psi_{\min} \leqslant \psi \leqslant 2\pi - \psi_{\min}$$

where $\psi_{\min}$ can be found from the equation $\sin(\psi_{\min}/2) = \sin\theta \sin(\pi/N_2)$, where θ is the angle between C_{N_2} and C_∞. Therefore, with the exception of the case $\theta = \pi/2$, $N=2$, when the interval for ψ contracts into the point $\pi/2$ or to a multiple of it, it is always possible by a corresponding rotation around C_∞ to give ψ a value immeasurable with $2\pi/s$ $(s=1, 2, \ldots r)$, or equal to $2\pi/(r+s)$, which leads to C_∞. Thus, the statement is proved.

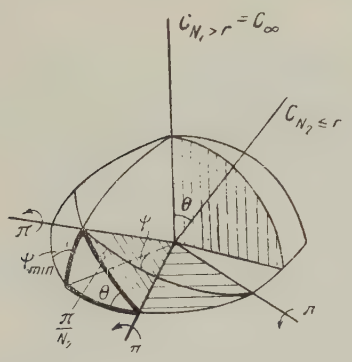
For the direct analytic proof of this theorem in the case of an arbitrary r $(N_1 > r)$ it is sufficient to prove it for $C_{N_1>r} = C_\infty$ and C_2, to which the general case C_∞ and C_{N_2} can always be reduced by replacing the rotation of $2\pi/N_2$ by two rotations of π around the two axes which form the angle π/N_2. Let (3) be directed along $C_{N_1>r} = C_\infty$. Then in the system of axes (1, 2, 3) the components of the tensor $S_{i_1 i_2 \ldots i_r}$ $(i_1, i_2, \ldots i_r = 1, 2, 3)$ with rank r that are compatible with the symmetry C_∞ will have the form as shown in considering the general case. Substituting them in the expression $S_{i'_1 i'_2 \ldots i'_r} = \alpha_{i'_1 i_1} \alpha_{i'_2 i_2} \ldots$

$\ldots\ \alpha_{i_r' i_r} S_{i_1 i_2 \ldots i_r}$, we shall get:

$$S_{i_1' i_2' \ldots i_r'} = \sum_P A^P \delta_{i_1' i_2'} \ldots \delta_{i_{r-1}' i_r'} + \ldots + \sum_P \underbrace{A^P_{3\ldots3}}_{r-2} \alpha_{i_1' 3} \alpha_{i_2' 3} \ldots \alpha_{i_{r-2}' 3} \delta_{i_{r-1}' i_r'} +$$

$$+ \alpha_{i_1' 3} \ldots \alpha_{i_r' 3} \underbrace{A_{3\ldots3}}_{r}$$

Choosing the axis $(1' \perp (3)$ and $(3')$, and taking into account that, in view of $C_2 \parallel (3')$, all the components $S_{i_1' i_2' \ldots i_r'}$ containing $(3')$ vanish an odd number of times, it is not difficult to prove that at $\alpha_{2'3} = \cos\theta \neq 0$ $(\theta \neq \pi/2,\ {}^3/_2\pi)$ all the terms in the right-hand part are zero, except the first sum. Indeed, putting for instance, $i_1' = 2'$, $i_2' = 3'$, $i_3' = \ldots = i_r' = 1$, we obtain in virtue of $\alpha_{1'3} = 0$ and $\delta a_1 a_2 = \begin{cases} 1, a_1 = a_2 \\ 0, a_1 \neq a_2 \end{cases}$, $\alpha_{23}\alpha_{33} \underbrace{A^P_{3\ldots3}}_{r-2} =$



$= 0$ for P equal to $\begin{pmatrix} i_1' i_2' i_3' \ldots i_r' \\ 1\,3\,1 \ldots 1 \end{pmatrix}$. The last is evidently true for all the possible transpositions P $(2, 3, 1, \ldots, 1)$; therefore the sum with the terms like $\underbrace{A^P_{3\ldots3}}_{2-r}$ vanishes; then putting $P\,(2, 3, 3, 3, 1, \ldots, 1)$ we find respectively: $\underbrace{A^P_{3\ldots3}}_{r-4} = 0$, *etc.* So, $S_{i_1' i_2' \ldots i_r'} =$

$= \sum_P A^P \delta_{i_1' i_2'} \ldots \delta_{i_{r-1}' i_r'}$, whence the isotropy follows immediately.

So for the crystals the classes of octahedra O (C_3 and C_4) and the tetrahedron T (two axes C_3 combined) are isotropic relative to the properties $r = 0, 1, 2$. The space isotropy for the properties with $r > 2$ does not follow from the symmetry of the crystals, as the possibility of combinations in them of axes of higher order than C_3 and C_4 is excluded (if we leave out of consideration $C_2 \perp C_N$, $N = 1, 2, 3, 4, 6$, which only leads to the bilateral axis; the properties with $r = 3$ for O disappear in consequence of C_i). For the molecules, the presence of icosahedron groups (C_5 and C_3 combined) makes the space isotropy possible for the properties up to $r = 1, 2, 3, 4$.

Physical-Technical Institute.
Academy of Sciences of the Ukrainian SSR.
Kharkov State University.

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PHYSICS

ON THE STRUCTURE OF THE PRINCIPAL SCATTERING LINE AND THE NATURE OF CONTINUOUS RADIATION

By M. F. VUKS

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The resonance filter method makes it possible, as has been shown in an earlier paper (1), to study in detail the intensity distribution in the Rayleigh line starting with very short distances from the centre (of the order 0.5 cm^{-1}). Besides benzene, which was reported on earlier, we have also studied carbon disulphide

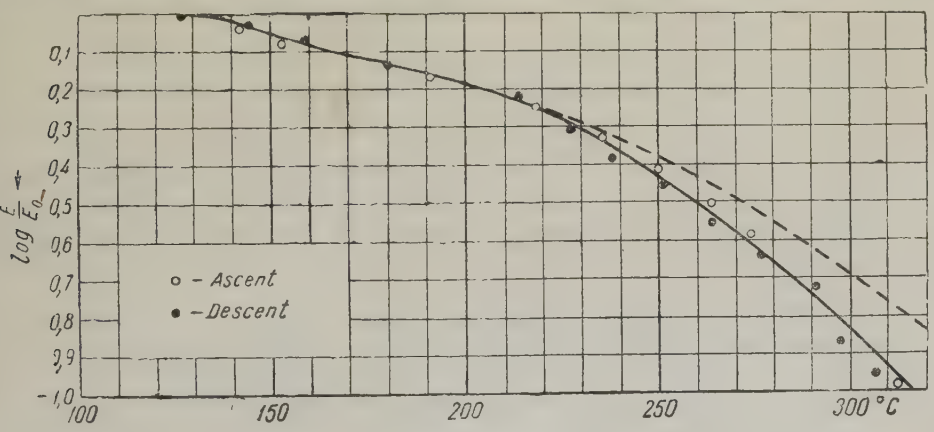

Fig. 1

with analogous results. The experimental conditions were the same. In Fig. 1 plot is given of the passage of sodium light scattered by carbon disulphide through the absorption tube as a function of temperature.

This curve roughly resembles the one for benzene. Here, too, the intensity slowly decreases as the absorption pit broadens. However, there are some essential differences in detail. In carbon disulphide the decrease in intensity of the light passing through the filter decreases slower at the outset and more rapid at the end than in benzene.

The intensity distribution was calculated by the same method as before, the following table being used us a basis.

T, °K	M (in cm^{-1})	E/E_0
430	0.0491	0.820
460	0.319	0.687
490	1.63	0.566
520	6.82	0.424
550	24.3	0.2864
580	75.7	0.1770

$K = 0.0626;\ 0.25;\ 1;\ 4;\ 16;\ 64;\ 256$

Then the following values were obtained for the amplitudes of the seven intensity functions summed up: -1; $+2.998$; $+1.734$; $+0.7238$; -0.1504; $+0.1322$; -0.01577. The function is graphically represented in Fig. 2.

From 420 to 600° K the calculated and experimental curves $E/E_0 = f(T)$ coincide up to small fractions of a per cent (Fig. 1). Hence the calculated curve represents the shape of the scattering line of carbon sulphide with sufficient accuracy (Fig. 2). This curve is very similar to the one for benzene. Here also there is a maximum at 1.5 cm^{-1}, only it is less distinct.

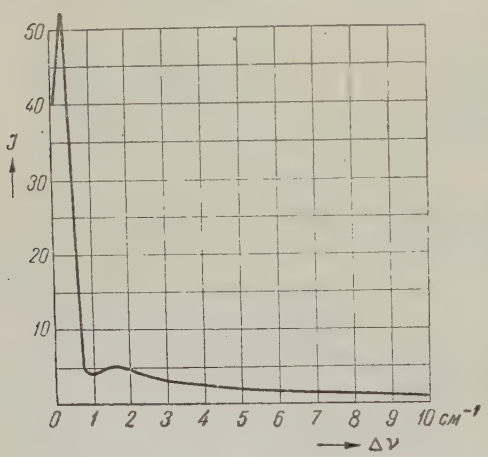

Fig. 2

Besides these substances, carbon tetrachloride, hexane and optical (crown) glass were also investigated, although less thoroughly. The curves for the passage of light for carbon tetrachloride and hexane differ markedly from those for benzene and carbon disulphide. Here they fall very abruptly. This indicates that the intensity of the modified radiation falls off rapidly with distance from the centre of the line. Nearly $^9/_{10}$ of the full brightness is concentrated in the narrow central line. The wings account for no more than $^1/_{10}$ of the full radiation. In the case of benzene and carbon disulphide the wings account for $^1/_2$ and $^2/_3$ of the full radiation, respectively.

It is of interest to examine the results obtained with glass, where continuous radiation was also observed near the central line. Since this radiation is weak, it was difficult to detect it by the usual spectroscopic methods because of the presense near the central line of a background due to parasitic phenomena. The curve for the passage of light through the filter falls still more abruptly for glass than for carbon tetrachloride, but deviates appreciably from the curve for direct light.

Now we can affirm with greater reason than before that the wings near the Rayleigh line are not a unique property of the liquid and gaseous states. The detection of this effect in silica glass raises new great difficulties for the old hypothesis, which ascribes the effect in liquids to the rotation of the molecules.

Elsewhere ([2]) we advanced a new explanation of this effect according to which it is due to the intermolecular oscillations within the quasi-crystalline structure similar to the lattice oscillations of a crystal. The outer part of the wings, beginning with 10—20 cm^{-1}, is in good agreement with this explanation, since a tangible relation is observed between the continuous spectrum of the liquid and the low frequency lines of the crystal.

However, since the indicated lines of the crystals are due chiefly to the rotational oscillations of the molecules in the lattice, it follows that the outer part

of the wings of the Rayleigh line in liquids is also due chiefly to the rotational oscillations of the molecules.

It now seems possible to explain the central part of the wings in a similar manner. I conceive this phenomenon as follows.

Thermal agitation in liquids may evidently be thought in general, as in crystals, as the superposition of acoustical waves in all possible directions from a frequency close to zero to the limiting frequencies. However, there must be some differences here, too. First of all, it is clear that the spectrum of transverse waves and of waves of the rotational oscillations cannot extend far to the low-frequency side. Secondly, in liquids with anisotropic molecules there should exist in small volumes unhomogeneities due to the different orientation of the molecules in diverse elements of the volume. This follows from the quasi-crystalline structure of the liquids. It is clear that the short Debye waves must be highly dispersed on these unhomogeneities and therefore rapidly damped, so that their propagation should be restricted to small distances. The dimensions of these anisotropic volumes are determined by the distances to which the congruity in the disposition of the molecules extends.

The singularities in the thermal agitation of liquids should have their effect on the picture of light scattering. The light scattered in different elements of volume on short Debye waves is incapable of interference and, therefore, as distinct from crystals, should appear with considerable intensity in the form of slightly modified radiation adjacent to the principal line. The intensity distribution should depend on the dimensions of the anisotropic regions. Of greatest significance here should be the oscillations that are connected with the change in anisotropy in the small volumes.

Thus, the central part of the continuous radiation, as well as the outer part, should be explained by intermolecular oscillations of the same type as lattice oscillations, the only difference being that if the outer part belongs to the optical branch, the central one belongs to the acoustical branch.

The L. V. Pissarjevsky Institute of Physical Chemistry, Kiev.
Academy of Sciences of the Ukrainian SSR.

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PHYSICS

ON THE DETERMINATION OF THE FREE SURFACE ENERGY OF CRYSTALS

By V. K. SEMENCHENKO

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§ 1. Until now we do not have a single sufficiently reliable method for experimentally determining or theoretically computing the free surface energy of solids, the analogue of the surface tension of liquids, although numerous attempts have been made in this direction in view of its extreme importance. Here a method is proposed that has the advantage of being rigorously grounded. Its chief shortcoming is the narrow temperature range in which it is applicable.

Let us derive the formulae determining the vapour pressure of a small crystal. We will consider a system consisting of a single crystal in equilibrium with its own vapour, and determine its equilibrium conditions when the total volume and the temperature are constant. In so doing we will assume that the surface area of the crystal can change only if the volume changes. Then

$$F = \sum \sigma_i s_i + f' + f'' \tag{1,1}$$

where F is the free energy of the entire system; f', the free energy of the single crystal; f'', the free energy of the vapour; s_i, the areas of the crystal faces; σ_i, their free surface energies. Moreover,

$$V = V' + V'' = \text{const}, \quad N = n' + n'' = \text{const} \tag{1,2}$$

V^j is the volume of the j-plase; n', the number of molecules in the phase.

At equilibrium, $F = F_{\min}$, and hence:

$$\delta F = \sum \sigma_i \delta s_i + \mu' \delta n' + \mu'' \delta n'' - p' \delta V' - p'' \delta V'' = 0 \tag{1,3}$$

and in accordance with (1,2)

$$\delta V = 0 = \delta V' + \delta V''; \quad \delta N = 0 = \delta n' + \delta n'' \tag{1,4}$$

As usual, although this is rather an approximation (1), we will regard the volume of the crystal as the sum of the volumes of pyramids where altitu-

des l_i are perpendiculars dropped from the crystal of the crystal t o its Then:

$$V' = \frac{1}{3}\sum s_i l_i, \quad \delta V' = \frac{1}{2}\sum l_i \delta s_i \tag{1,5}$$

Under conditions (1,4) and (1,5), expression (1,3) now becomes:

$$\delta F = \sum \left\{ \sigma_i - \frac{1}{2} l_i (p' - p'') \right\} \delta s_i + (\mu' - \mu'') \delta n' = 0 \tag{1,3'}$$

In (1,3') the variations δs_i and $\delta n'$ are independent, and hence:

$$\sigma_i - \frac{1}{2} l_i (p' - p'') = 0 \quad \text{or} \quad p' - p'' = \frac{2\sigma_i}{l_i} \tag{1,6}$$

and

$$\mu' = \mu'' \tag{1,7}$$

By definition the chemical potential

$$\mu = (u - Ts + pV)/n$$

where u is the internal energy; T, the temperature; s, the entropy; p, the pressure; V, the volume; and n, the number of molecules of the given (one-component) phase. Therefore, taking into account (1,6), we may write (1,7) thus:

$$\frac{u' - Ts' + p'V'}{n'} + 2\,\frac{\sigma_i V'}{l_i n'} = \mu'' \tag{1,7'}$$

and since by definition the first member on the left-hand side of (1,7') is $\mu'_{p''}$, *i. e.*, μ' at a pressure p'', and V'/n' is the effective volume of one molecule v'_m, we have

$$\mu'_{p''} + 2\,\frac{\sigma_i v'_m}{l_i} = \mu'' \tag{1,7''}$$

Substituting the usual expression for μ we get:

$$\mu'_0 + kT \ln f'_a c' + 2\,\frac{\sigma_i v'_m}{l_i} = \mu''_0 + kT \ln f''_a c'' \tag{1,8}$$

where f_a^j are the activity coefficients, and c^j, the volume concentrations of the substance in the phase j. Since for not very small crystals c' and f'_a do not depend upon the volume, when $l \to \infty$ we will get:

$$\mu'_0 + kT \ln f'_a c' = \mu''_0 + kT \ln f''_{a\infty} c''_\infty \tag{1,8'}$$

Subtracting (1,8') from (1,8) and keeping in mind that for a gaseous phase $f'_{a\infty} \approx f''_a \approx 1$, we find that

$$c'' = c''_\infty e^{2\sigma_i V'_m / l_i RT} \tag{1,9}$$

where V'_m is the molar volume.

Highly essential is the fact that in accordance with (1,6) we have:

$$\frac{\sigma_i}{l_i} = \text{const} = W \tag{1,10}$$

since the value of the ratio σ_i/l_i does not depend upon l. Since the constant W was introduced by Wulf, we will call it the Wulf constant. Hence

$$c'' = c''_\infty e^{2WV'_m/RT} \tag{1,9'}$$

When all virtual and real σ are equal, the crystal becomes a sphere, and equation (1,9) reduces to the Kelvin equation for a drop

$$c'' = c''_\infty e^{2\sigma V'_m / rRT} \tag{1,9''}$$

where r it the radius of the drop.

At the melting point the concentrations of the saturated vapour are equal for both phases. Therefore

$$c'' = c''_\infty e^{2\sigma_i V'_m / l_i RT} = c''_\infty e^{2\sigma'' V'_m / rRT} = c''_\infty e^{2WV'_m/RT} \tag{1,11}$$

Whence

$$\sigma'_i = \sigma'' \frac{V'^{-1}_m}{V''^{-1}_m r}; \quad W = \frac{\sigma'' V''_m}{rV'_m} \tag{1,11'}$$

At a sufficiently small vapour concentration (which is nearly always the case at the melting point) these relations hold exactly. T is the melting point of the crystal or drop of given dimensions, which somewhat extends the range of application of (1,11').

For cubes we have

$$8l^3\rho' = \frac{4}{3}\pi r^3 \rho''$$

and as

$$\frac{V''_m}{V'_m} = \frac{\rho'}{\rho''}$$

always, therefore

$$\sigma' = \frac{\sigma''\rho'}{\rho''}\sqrt{\frac{4\pi\rho''}{3\cdot 8\rho'}} = \sigma''\sqrt[3]{\frac{\pi}{6}}\left(\frac{\rho'}{\rho''}\right)^{2/3} \tag{1,12}$$

We can also find the value of the Wulf constant for both phases:

$$W'V'_m = W''V''_m = \frac{\sigma''}{r}V''_m \tag{1,13}$$

$$\frac{W'}{W''} = \frac{\rho'}{\rho''} \tag{1,13'}$$

$$W' = \frac{\sigma''}{r}\frac{V''_m}{V'_m} = \frac{\sigma''}{r}\frac{\rho'}{\rho''} \tag{1,13''}$$

Hence the Wulf constants are to each other as the densities of the two phases. It is therefore clear that except for faces with $l_i \gg r$, σ' is always of the same order as σ'', the surface tension of the liquid phase.

So in rough computations the values σ' may be used for σ'' in the neighbourhood of the melting point. It is interesting that for anomalous substances for which $V'_m > V''_m$ such as H_2O, Bi and Sb, σ', at least for some faces, will be less than σ''. Equations (1,11)—(1,13'') point to the existence of an intimate relation between the molar volume or the density and the surface tension upon transition from one state of aggregation to another, and therefore probably existing also in one and the same state at different temperatures.

§ 2. The method may also be applied to multi-component crystals, which are solid solutions. In this case we have for the free energy of the system single crystal—vapour or diluted solution (here we take a two-component system for simplicity):

$$F = \sum s_i \psi_i + f' + f'' \tag{2,1}$$

where ψ is determined according to Gibbs: $\psi = \sigma + \mu\Gamma$; $\Gamma = \delta(c_s - c' - c'')$; Γ, the adsorption; c_s, the concentration of the admixture at the interface; and c' and c'', its concentrations in the volume phases. Moreover,

$$V' + V'' = V = \text{const}; \quad V' = \frac{1}{3}\sum s_i l_i; \quad N_0 = n'_0 + n''_0;$$

$$N_1 = n'_1 + n''_1 + \sum s_i \Gamma_i \tag{2,2}$$

The general equilibrium condition is:

$$\delta F + \sum (\psi_i \delta s_i + s_i \delta \psi_i) + \sum_j (\mu_0^j \delta n_0^j + \mu_i^j \delta n_i^j) - p' \, dV' - p'' \, dV'' \qquad (2,3)$$
$$\delta V' + \delta V'' = 0; \quad \delta N_0 = \delta n_0' + \delta n_0'' = 0$$

and

$$\delta N_1 = \delta n_1' + \delta n_1'' + \sum (s_i \delta \Gamma_i + \Gamma_i \delta s_i) \qquad (2,4)$$

whence

$$\delta F = \sum (\psi_i \delta s_i + s_i \delta \psi_i) + (\mu^{0\prime} - \mu^{0\prime\prime}) \, \delta n_0' +$$
$$+ (\mu_1' - \mu_1'') \, \delta n_1'' - \mu_1'' \sum_i (s_i \delta \Gamma_i + \Gamma_i \delta s_i) - (p' - p'') \, \delta V' = 0 \qquad (2,3')$$

But $\delta \psi_i = \mu_i \delta \Gamma_i$ and $\delta V' = {}^1/_2 \, \Sigma l_i \cdot \delta s_i$. Therefore:

$$\delta F = (\mu^{0\prime} - \mu^{0\prime\prime}) \, \delta n_0' + (\mu_1' - \mu_1'') \, \delta n_1' + \sum \left[\sigma_i - \frac{1}{2} l_i (p' - p'') \right] \delta s_i = 0 \qquad (2,3'')$$

In equations (2,3″) all variations are independent, and hence:

$$\mu^{0\prime} = \mu^{0\prime\prime}; \quad \mu_1' = \mu_1'' \qquad (2,5)$$
$$p' - p'' = 2 \frac{\sigma_i}{l_i} \qquad (2,6)$$

and as a consequence of (2,6):

$$\frac{\sigma_i}{l_i} = W = \text{const} \qquad (2,7)$$

where W, as before, is the Wulf constant.

Proceeding in the way we did in deriving (1,8), we get

$$c_k'' = \frac{f_k'}{f_k''} c_k' k_0 e^{2\sigma_i V_k'/l_i RT} = \frac{f_k'}{f_k''} c_k' k_0 e^{2WV_k'/RT} \qquad (2,8)$$

and analogously to (1,9)

$$c_k'' = c_{k\infty}'' e^{2WV_k'/RT} = c_{k\infty}'' e^{2\sigma_i V_k'/l_i RT} \qquad (2,9)$$

For a drop of equal mass we have at the melting point:

$$c_{km}'' = c_{km\infty}'' e^{2\sigma V_{km}'/rRT} \qquad (2,10)$$

and since $c_{km}'' = c_k''$

$$W_k = \frac{\sigma_i}{l_i} V_k' = \frac{\sigma}{r} V_{km}' \qquad (2,11)$$

Hence in this case too W and σ_i can be computed if σ, r, V_k' and V_{km}' are known. Our method makes it possible to compute σ_i at the solution crystal interface as well, if σ is known. To the author's knowledge, no one has ever suggested a method for the approximation of this quantity.

It is clear that σ_i will be a magnitude of the same order as σ for a drop.

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HEAT ENGINEERING

HEAT EXCHANGE BETWEEN A PLATE AND A FLOW OF GAS MOVING PAST IT IN LONGITUDINAL DIRECTION

By Z. F. CHUKHANOV, Corresponding Member of the Academy

The problem of heat exchange between a gas flow and a flat plate oriented along the flow presents the simplest case of the so-called «external problem».

Approximate equations of a laminar boundary layer for a plate oriented along the flow have been solved by Pohlhausen (1). For the coefficient of heat transfer $\varphi = \mathrm{Nu}_x/\mathrm{Pe}_x$ he obtained the following equation:

$$\varphi = 0.664 \mathrm{Re}_x^{-1/2} \mathrm{Pr}^{-2/3} \tag{1}$$

where $\mathrm{Pe}_x = \mathrm{Re}_x \mathrm{Pr} = \frac{w_m x}{\nu} \frac{\nu}{a} = \frac{w_m x}{a}$; $\mathrm{Nu}_x = \frac{\alpha x}{\lambda_g}$; w_m, the velocity of the incoming flow; α, the coefficient of heat exchange; λ_g, the thermal conductivity of the fluid; a, thermometric conductivity; ν, kinematic viscosity. The coordinate x is defined to be directed along the surface. Piercy and Schmidt (2) and also Kruzhilin (3) have obtained for φ an equation analogous to (1).

An attempt to obtain a theoretical solution of the problem for a turbulent boundary layer of gas by analogy with the internal problem was made by Sknar (4). He proceeded on the basis of Reynolds' hydrodynamical theory of heat exchange. Latzko (5) has investigated the heat exchange between a plate and a turbulent flow (for $\mathrm{Pr} = 1$) and obtained the following equation

$$\varphi = 0.0256 \ \mathrm{Re}^{-0.2} \tag{2}$$

Upon analysing the heat exchange in a channel (6) the present author found that neither the equation of the hydrodynamical theory of Reynolds-Prandtl-Karman, nor the equation of Latzko, which practically coincides with the former, give a sufficient agreement with the experiment, even for the simplest case of heat exchange with gas. The equation which the author (6) has obtained for heat exchange in a channel ($\mathrm{Pr} = 1$) has the following form:

$$\mathrm{Nu} = \frac{\zeta}{4} \frac{\mathrm{Re}}{1 + \frac{w_1}{\bar{w}} \left(2 - \frac{w_1}{\bar{w}} \right)} \tag{3}$$

where the ratio $w_1/\bar{w}$ is uniquely determined from the well-known equation (7,8)

$$\frac{w_1}{\sqrt{\tau/\rho}} = 10.45; \quad \frac{w_1}{\bar{w}} = 3.7 \sqrt{\zeta} \tag{4}$$

In the case of a liquid for $\mathrm{Pr} \neq 1$, equation (3) because of lack of similarity between the velocity field and the temperature field can be written in the following form, if no allowance is made for the variation of ζ with Pr:

$$\mathrm{Nu} = \frac{0.25\,\zeta\,\mathrm{Re}\,f(\mathrm{Pr})}{1+7.4\sqrt{\zeta}-13.7\zeta} \tag{5}$$

The magnitude of the Prandtl number virtually determines the relation between the boundary hydrodynamic layer and the heat layer. With large values of Pr the temperature in the region of the turbulent core is constant, and Nu_{pr} for a channel is obviously determined by the relation

$$\mathrm{Nu}_{pr} = \frac{d}{\delta_p} = 0.0191\ \mathrm{Re}^{7/8} \tag{6*}$$

Comparisons of the experimental data with the equation (6) show that δ_p, the thickness of the pseudolaminar layer, and also ζ both vary with Pr, though this variation seems to be slight. Some later works give a corroborative evidence to this effect (9).

The theoretical determination of $f(\mathrm{Pr})$ in equation (5) will be the subject of a special investigation. Since for a gas $\mathrm{Pr} = 0.72$, *i. e.* is near to unity, no appreciable error will be introduced, if, in comparing equation (5) with the experimental data on heat exchange in a gas the influence of Pr is assumed, as usual, to coincide with the empirical relation established for a turbulent boundary layer. Then equation (5) for heat exchange in a channel can be written down in the following form, suitable for computation *:

$$\varphi = \frac{0.25\,\zeta\,\mathrm{Pr}^{-2/3}}{1+7.4\sqrt{\zeta}-13.7\zeta} \tag{6}$$

For a gas we have

$$\varphi = \frac{0.309\zeta}{1+7.4\sqrt{\zeta}-13.7\zeta} \tag{7}$$

For determining φ in a channel of slit-like cross-section we have (in determining ζ) to take for the characteristic dimension $d_e = 2b$, *i. e.* the double width of the slit. Seeing that for $\mathrm{Pr} \sim 1$ the temperature field in a flow past a plate is similar to the velocity field, the problem of heat exchange between the gas and the plate can be approximately reduced to that between a gas and a wall of a slit-like or circular channel

$$d_e = 2b = 4\delta_t$$

Thus

$$d_e = 1.48x\mathrm{Re}_x^{-1/5} \quad \text{for} \quad \mathrm{Re}_x = \frac{w_m x}{\nu} \tag{8}$$

and for the conditions under which Blasius' law is valid:

$$\zeta_p = 0.3164 / \mathrm{Re}^{0.25} = 0.296\ \mathrm{Re}_x^{-1/5} \tag{9}$$

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*A point that needs to be cleared up is to which region of the flow should we refer ν in determining ζ from Blasius' equation. According to Mikheev (11) $\zeta = \frac{0.316}{\mathrm{Re}^{1/4}} \frac{\mathrm{Pr}_w^{1/3}}{\mathrm{Pr}_f}$.

As in this case *

$$\mathrm{Re} = 1.295\ \mathrm{Re}_x^{4/5} \tag{10}$$

and

$$\bar{w} = \frac{1}{\delta_r}\int_0^{\delta} w\left(\frac{y}{\delta}\right)^{1/7} dy = \frac{7}{8}\, w_m \tag{11}$$

therefore the local value of the coefficient of heat transfer φ_p^* for a plate is determined by the equation

$$\varphi_p^* = \frac{0.27\ \zeta_p}{1+7.4\sqrt{\zeta_p}-13.7\,\zeta_p} = \frac{0.08\ \mathrm{Re}_x^{-0.2}}{1+4.02\,\mathrm{Re}_x^{-0.1}-4.05\,\mathrm{Re}_x^{-0.2}} \tag{12}$$

$$\mathrm{Nu}_x^* = \frac{0.058\ \mathrm{Re}_x^{0.8}}{1+4.02\,\mathrm{Re}_x^{-0.1}-4.05\,\mathrm{Re}_x^{-0.2}} \tag{13}$$

Upon integrating and rounding off the figures for an interval of Re_x from 10^5 to 10^6 we obtain an approximate expression which determines the average value of $\overline{\overline{\mathrm{Nu}}}_x$ from 0 to x:

$$\overline{\overline{\mathrm{Nu}}}_x \approx 0.028\,\mathrm{Re}_x^{0.826} \tag{14}$$

The value of $\overline{\overline{\mathrm{Nu}}}_x$ determined from equation (14) correspondingly determines the value of $\bar{\bar{\alpha}}$ referred to the mean temperature head $\bar{\vartheta}$, whereas it is customary for the external problem to refer α to the maximum temperature head ϑ_m.

By definition, $\bar{\vartheta}$ can be obtained from the following relation

$$\bar{\vartheta} = \frac{\int_F \vartheta w\, dF}{\int_F w\, dF} \approx 0.89\ \vartheta_m \tag{15}$$

A refined value of $\bar{\vartheta}$ can be determined from the balance equation and from equation (14):

$$\frac{\bar{\vartheta}}{\vartheta_m} = 1 - \frac{Q_1}{Q_0} = 1 - \frac{\overline{\overline{\mathrm{Nu}}}_x \dfrac{\vartheta}{\vartheta_m}\lambda}{0.326\ c_p w_m\ \mathrm{Re}_x^{-0.2}\, x} \tag{16}$$

Finally, the equation of heat exchange for a plate is obtained in the following form:

$$\mathrm{Nu}_x \approx \frac{0.028\,\mathrm{Re}_x^{0.826}}{1+0.15\,\mathrm{Re}_x^{0.005}} \approx 0.0244\ \mathrm{Re}_x^{0.826} \tag{17}$$

Equation (17) corresponds to a completely turbulent boundary layer

$$\varphi_p \approx 0.0336\ \mathrm{Re}_x^{-0.175} \tag{18}$$

According to Elias ([10]), a turbulent boundary layer is formed when $\mathrm{Re}_x \sim 110\,000$ in the case of a rough ** surface and when $\sim 160\,000 - 180\,000$ in the case of a smooth surface.

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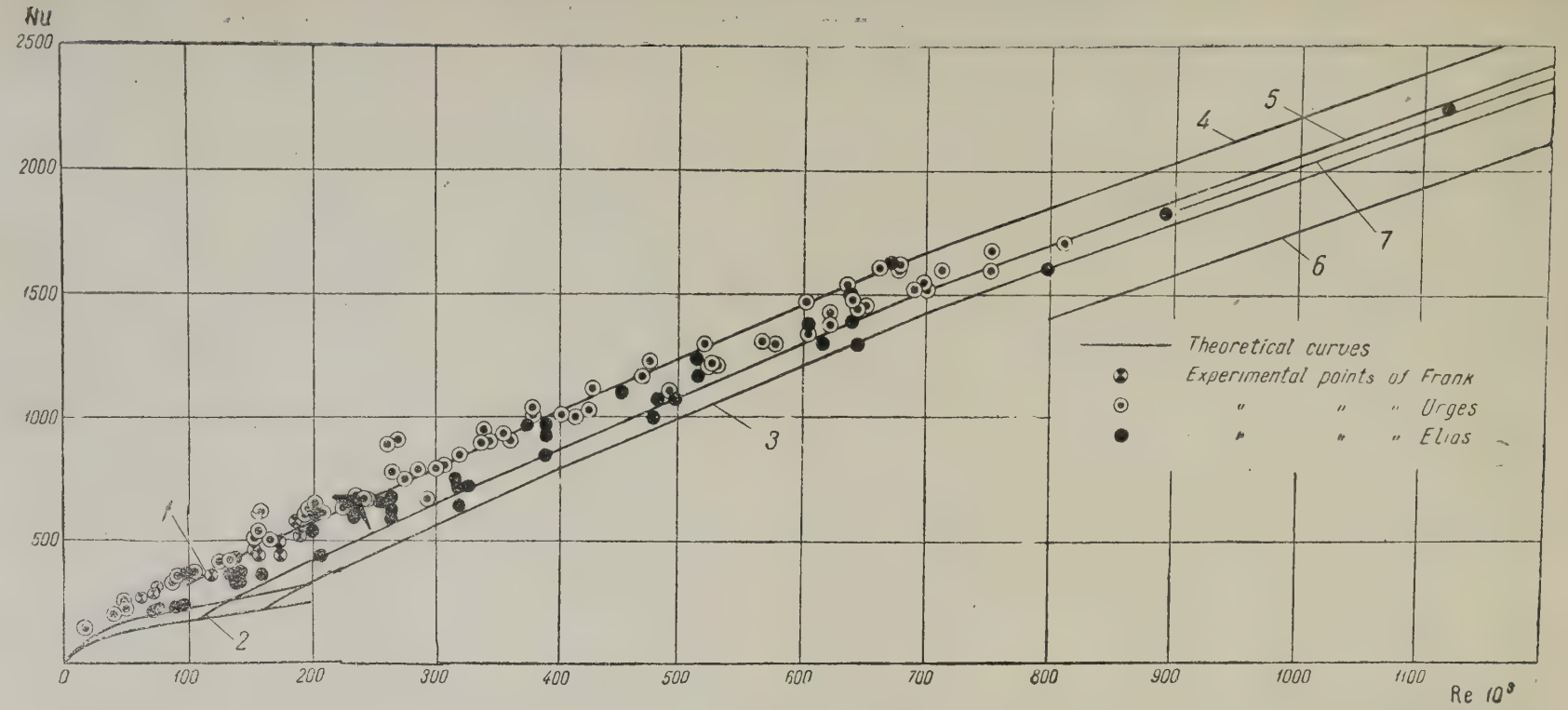
* It may be remarked that equation (8) also gives the expression for C_f (plate), a quantity often used in hydrodynamics

$$C_f = \zeta/4 = 0.074\,\mathrm{Re}_x^{-1/5}$$

This expression for C_f exactly coincides with the empirical equation.

** According to (10) this corresponds to $\mathrm{Re} \sim 15\,000$, which in the case of a slit-like channel corresponds closely to the values at which a turbulent regime sets in; see Marx, experiments ([11]).



1, according to Piercy and Schmidt's equation $Nu = 0.73\ Re$; 2, according to Kruzhilin's equation $Nu = 0.60\ Re^{0.5}$; 3, according to author's equation $Nu_x \approx 0.0244\ Re^{0.8\cdot6}$—256; 4, according to author's equation $Nu_x \approx 0.0244\ Re_x^{0.8\cdot26}$; 5, according to author's equation $Nu_x \approx 0.0244\ Re_x^{0.8\cdot26}$—153; 6, according to Latzko's equation $Nu = 0.032\ Re^{0.8}$—256; 7, according to Latzko's equation $Nu \approx 0.032\ Re^{0.8}$

Thus, for a plate with a smooth surface and for $\mathrm{Re}_x < 170\,000$, the value of φ_p is determined from equation (1)

$$\varphi_p = 0.83\ \mathrm{Re}_x^{-0.5} \tag{19}$$

for $\mathrm{Re}_x > 170\,000$ we have

$$\varphi_p \approx \frac{0.0336\ \mathrm{Re}_x^{0.826} - 360}{\mathrm{Re}_x} \tag{20}$$

and, finally, for rough plates, for which a turbulent boundary layer develops at $\mathrm{Re}_x \sim 110\,000$, we have

$$\varphi_p \approx \frac{0.0336\ \mathrm{Re}_x^{0.826} - 210}{\mathrm{Re}_x} \tag{21}$$

Correspondingly, the equations analogous to (17) are:

$$\mathrm{Nu}_p = 0.6\ \mathrm{Re}_x^{0.5} \tag{19*}$$

$$\mathrm{Nu}_p \approx 0.0244\ \mathrm{Re}_x^{0.826} - 256 \tag{20*}$$

$$\mathrm{Nu}_p \approx 0.0244\ \mathrm{Re}_x^{0.826} - 153 \tag{21*}$$

Equations (19), (20), (21) and (19*), (20*), (21*) can be applied in practical calculations both to heat-exchange processes and diffusion processes. Just how close is the agreement between the established theoretical equations and the experimental results in the case of a plate (a range), is shown by the figure.

The theoretical curves have been plotted according to (19*), (20*) and (21*), and also according to Latzko's equations: a) for the turbulent layer and b) taking into account the laminar region on a smooth plate. The experimental points correspond to the data obtained by Frank, Urges ([11]) and Elias ([10]). Elias' data have the advantage of being obtained under conditions where the initial unheated portion of the range had the least possible area. In the experiments performed by Urges a turbulent boundary layer was observed practically always, and the initial unheated area of the range being considerable, the results for Nu are probably somewhat overestimated.

As may be seen from the figure, the curve representing equation (20*) satisfactorily describes the data obtained by Elias. The scattering of his points may be accounted for by the complexity of his procedure. It should be noted that for practical purposes it is more convenient to determine instead of Nu, the value of φ, the coefficient of heat transfer (or matter transfer, in the case of diffusion). For instance, solving the Fourier-Kirchhoff equations for a channel when t_0 (temperature of the wall) is constant, the regime stationary, the temperature of the gas along the channel can be determined from the following simple equation, if the thermal conductivity of the gas along the wall is neglected:

$$t = t_0 \left(1 - \exp \varphi \frac{l}{d}\right) \tag{22}$$

A similar method can be used in determining the gas component discharge curve in the case of burning coal channel, or for any other reaction taking place at the surface.

The Tbilissi Institute
of Railway Engineers.

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CHEMISTRY

A DINUCLEAR INTERNAL COMPLEX SALT OF CHROMIUM AND GLYCINE AND ITS SPLIT PRODUCTS

By L. M. VOLSTEIN

(Communicated by V. G. Chlopin, Member of the Academy, 19.IX.1944)

The predominant product which forms in the reaction between hydrated chromium chlorides and glycocole is a diglycine derivative with the empiric formula $Cr(NH_2CH_2COO)_2CH$.

This compound was first described in 1910 in a paper by Chugaev and Serbin(1), in which the authors made the assumption that the formula should probably be doubled, and that it possibly has the following structure:

$$[(NH_2CH_2COO)_2\,Cr\begin{matrix}OH\\OH\end{matrix}Cr\,(NH_2CH_2COO)_2]$$

The authors, however, stressed the fact that this assumption had yet to be verified by further investigations. In 1912 Ley and Ficken produced this same compound (2) and mentioned that one of following formulae might be assigned to it:

$$[CrGl_2\,(OH)\,H_2O]^* \qquad (I)$$

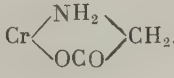
or

$$[Gl_2Cr\begin{matrix}OH\\OH\end{matrix}CrGl_2] \qquad (II)$$

The authors found that analysis data are closer to formula (II). However, it must be emphasized, that the authors analysed the substance in air-dry conditions and the data of their analyses correspond to the empiric formula $CrGl_2\,OH + \frac{1}{2}H_2O$, *i. e.* their data differed very little from those which should correspond to the hydroxy-aqua salt $[CrGl_2(OH)H_2O]$; the paper offers no proof of the structure assumed by the authors.

This paper gives experimental evidence of the fact that the substance in question belongs to the group of dinuclear internal complex salts; we have been able to prove this by splitting it with hydrochloric acid and isolating a number of

* The symbol Gl is used here to represent glycocole NH_2CH_2COO, which forms the following cyclic compound with the metal:



new compounds of individual interest, which are formed during this reaction.

Without going into a description of the method of producing $CrGl_2OH$ ([1, 2]) we shall mention only that the resulting violet-coloured precipitate was dried to constant weight at a temperature of 130°.

Careful analyses showed that the substance had a composition corresponding to the empiric formula: $CrGl_2OH$, and not the formula of the hydroxy-aqua salt $CrGl_2(OH)H_2O$, or of the crystallic hydrate $CrGl_2OH + \frac{1}{2}H_2O$, established by Ley and Ficken ([2]) for the air-dry substance.

Found %: Cr—24.02; 24.10; 24.07.

Calculated for $CrGl_2OH$ %: Cr—29.96.

This substance is practically insoluble in cold and hot water; it is insoluble also in dilute and moderately concentrated strong acids in the cold. But comparatively long boiling in dilute HCl results in the complete disappearance of the initial substance and in the formation of lilac-coloured solutions. The products of the reactions involved in this process are quite soluble in water and can be isolated only by evaporating the solutions dry. The author has carried out the following four sets of experiments.

1. A weighed portion (several tenths of a gram) of $CrGl_2OH$, mixed with 100—200 ml of water, was added with a definite volume (from a burette) of titred 0.1 *N* HCl. The volume was so calculated as to have exactly one mole of HCl to every mole of $CrGl_2OH$. After the mixture had been boiled for 30—40 minutes, the solid phase disappeared entirely, after which the resulting lilac-coloured solution was boiled down to a volume of several millilitres (upon which the colour became a very dark violet) and then was transferred to a weighed vessel. Further evaporation was conducted in a drying oven at a temperature of about 90°. Evaporating to dryness resulted in the formation of needle-like, dark violet, crystals which where dried to constant weight at 130°. Analyses of the substance gave figures, which corresponded well to the formula $[CrGl_2H_2OCl]$.

Found %: Cr—20.49; 20.41; 20.39; Cl—14.05; 14.20; 14.11.

Calculated for $(CrGl_2H_2OCl)$, %: Cr—20.51; Cl—13.96.

Evidently the reaction takes place according to the equation:

$$[(NH_2CH_2COO)_2\,Cr\begin{matrix}OH\\OH\end{matrix}Cr\,(NH_2CH_2COO)_2] + \begin{matrix}HCl\\HCl\end{matrix} \rightarrow$$

$$\rightarrow \left[(NH_2CH_2COO)_2\,Cr\begin{matrix}H_2O\\Cl\end{matrix}\right] + \left[\begin{matrix}Cl\\H_2O\end{matrix}Cr\,(NH_2CH_2COO)_2\right]$$

i. e. two molecules of the compound $(CrGl_2H_2OCl)$ are formed. Under the conditions described it is the two «ol-bridges», and not the glycocole cycles $\left(CH_2\begin{matrix}NH_2\\OCO\end{matrix}Cr\right)$ that are broken. The overweight of the vessel shows that the transformation is quantitative. The compound $(CrGl_2H_2OCl)$ is extremely hygroscopic, dissolves excellently in water and is insoluble in ethyl alcohol. If $AgNO_3$ is added to a freshly prepared solution of this compound, no precipitate appears at first, but after a moment AgCl begins to precipitate out gradually, or, if heated, very rapidly.

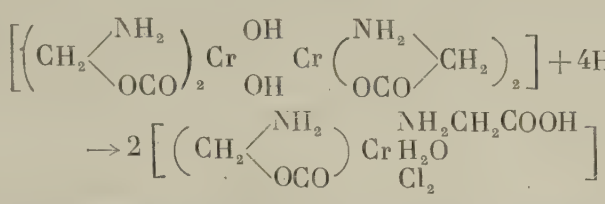
2. Analogous experiments were conducted in which 2 moles of HCl were added to each mole of $CrGl_2OH$. In this case evaporation resulted in the formation of beautiful, large needle-like crystals, green in colour, very hygroscopic, very soluble in water and, unlike the former substance, soluble in alcohol. Analyses

of the substance, dried to constant weight at 125°, showed that its composition corresponded to the formula $[CrGl(HGl)H_2OCl_2]$ *.

Found %: Cr—18.10; 18.13; Cl—24.30; 24.25.

Calculated for $[CrGl(HGl)H_2OCl_2]$, %: Cr—17.93; Cl—24.45

Thus, the action of two moles of HCl on 1 mole of $CrGl_2OH$ results not only in the breaking up of the ol-bridges, but in the breaking up of one of the glycocole cycles as well, according to the equation:

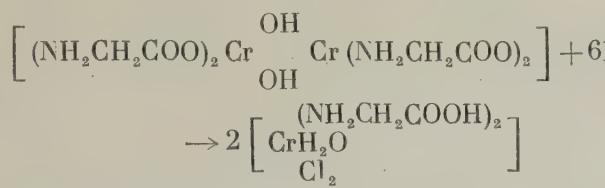


3. Analogous experiments were conducted in which 3 moles of HCl were added to each mole of $CrGl_2OH$. In this case evaporation resulted in the formation of green crystals similar in appearance and properties to the crystals produced in the former series of experiments (hygroscopic, very soluble in water and soluble in alcohol). Analyses of the substance dried to constant weight at 130° indicated the formula $[Cr(HGl)_2H_2OCl_3]$.

Found %: Cr—16.15; 16.07; Cl—32.52; 32.47.

Calculated for $[Cr(HGl)_2H_2OCl_3]$, %: Cr—15.93; Cl—32.58.

In this case the action of HCl results in the breaking up of the ol-bridges and both the glycocole cycles, according to the equation:



It should be mentioned that acting upon $CrGl_2OH$ with HCl in a greater molar proportion than 3 : 1, *e. g.* 4 : 1, was also tried, but, as might have been expected, the fourth mole of HCl refused to combine with the compound, and analysis showed that $[Cr(HGl)_2H_2OCl_2]$ was formed in this case, too.

4. The author was also successful in transforming the first split product ($CrGl_2H_2OCl$) into the second $[CrGl(HGl)H_2OCl_2]$, the second into the third $[Cr(HGl)_2H_2OCl_3]$, and the first—directly into the third. This was done by adding the required volume of 0.1 *N* HCl (calculating 1 or 2 moles HCl per 1 mole initial substance) from the burette into the vessel containing the first or second compound, evaporating the contents of the vessel in the drying oven at $t<100°$, and then drying to constant weight at $t=130°$. In all three cases the results were in accordance with expectation ($[CrGl_2H_2OCl]+HCl\rightarrow[CrGl(HGl)H_2OCl_2]$, *etc.*). There was always an overweight which coincided well within the limits of error with the theoretical calculations. The conclusions drawn from the overweight determinations were born out by analyses of the products.

It may also be mentioned that the addition of 0.1 *N* HCl to the third compound did not result in any overweight (after evaporation and drying) and, as analysis showed, did not affect the composition of the compound $[Cr(HGl)_2H_2OCl_3]$. The author was also able to bring about the reverse transformation quantitatively. The addition of 2 moles NaOH per one mole of $[Cr(HGl)_2H_2OCl_3]$ and one mole NaOH per one mole of $[CrGl(HGl)H_2OCl_2]$ results in the solutions turning from green to violet; subsequent addition of excess of alcohol results in the formation of a precipitate of the compound $[CrGl_2H_2OCl]$.

* The symbol HGl is used here to represent the glycocole molecule NH_2CH_2COOH.

So far we have not dealt with the stereochemistry of the compounds in question, nor with their physical-chemical properties; these problems are to be brought up in a future paper.

Up till now compounds with neutral glycocole molecules coordinated around the central atom were known to exist only with bivalent platinum; they were produced for the first time by Grünberg (3) and described in detail in papers by Grünberg and Volstein (4).

There are two papers in literature, by the way, published by biochemical laboratories, in which the authors (5,6) describe compounds produced by them, which they believe to have neutral glycocole molecules coordinated around the chromium atom. Thus, Florence and Couture (5), for instance, give the following formulae:

$$\left[Cr \begin{matrix} (H_2O)_2 \\ (C_2H_5NO_2)_4 \end{matrix} \right]^* \quad \text{or} \quad \left[Cr \begin{matrix} Cl \\ H_2O \\ (C_2H_5NO_2)_4 \end{matrix} \right] 2H_2O$$

It is easy to see that these formulae (as well as all the rest) are in gross contradictions with even the elementary requirements for the electrical neutrality of the molecules of these compounds, wherefore the conclusions drawn by the authors must be carrefully verified.

Conclusions. 1. A sequence of chromium diglycine derivatives has been produced, containing respectively 1, 2 and 3 chlorine atoms. All these compounds are non-electrolytes (meaning that all the component parts of the compound are in the internal sphere which has a zero charge), and the introduction of subsequent chlorines (Cl′) does not change the charge of the internal sphere, since simultaneously glycocole cycles are broken up, *i. e.* the radical $NH_2CH_2COO'(Gl')$ becomes a neutral molecule NH_2CH_2COOH.

2. It has been shown that the compound corresponding to the empiric formula $CrGl_2OH$ is a dinuclear internal complex salt with the following formula

$$\left[Gl_2Cr \begin{matrix} OH \\ OH \end{matrix} CrGl_2 \right].$$

Laboratory of Inorganic Chemistry.
The Kazan Institute for Chemical Technology.

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* These formulae are given exactly as they are in the paper named: $C_2H_5NO_2$ is the empiric formula for glycocole NH_2CH_2COOH.

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CHEMISTRY

THE SPECTRAL ABSORPTION OF COLOURED PHOSPHATE GLASSES AS A FUNCTION OF THEIR STRUCTURE

By V. P. DANILOV

(Communicated by I. V. Grebenshchikov, Member of the Academy, 6.IX.1944)

The lack of experimental data on coloured phosphate glasses has been a serious hindrance in the development of modern views on the nature of the colouring matter in them ([1–4]). Literature on spectral absorption available to-day deals mainly with silicate and boron silicate glasses of various compositions. We have undertaken a systematic investigation of the spectral absorption of some phosphate glasses, chiefly of the simplest composition («metaphosphates»), coloured by ions of cobalt, nickel, copper, iron, manganese, chromium and uranium.

Inasmuch as no direct methods are available determining the composition and structure of the colouring matter in glass, the method extensively used at present in investigations is a comparison of the spectral curves for solutions and glasses. If the character of the spectral absorption is the same, the chemical nature of the colouring matter in the glass is, by analogy, considered to be the same as that in the solution.

Although this method is only approximate, its use is justified by the prevailing theories on the structure of glass and liquids. More precise conceptions can be developed only if those structural properties of glass that distinguish it from solutions are taken into account.

In solutions the absorption spectra of the colouring matter change with the tendency of the various ions and polar molecules, which interact chemically with the ions of the colouring matter, to polarize. In glass the only type of ions capable of being highly polarized by the ions of the colouring matter are oxygen ions ([5]).

It may be assumed that variations in the absorption spectra for glasses having exactly the same colouring matter are due to different mutual polarization of the oxygen ions and those of the colouring matter, the mutual polarization depending on the degree to which the oxygen ions are polarized in the structural lattice of the glass.

In our investigations we have established that the spectral absorption of phosphate glasses varies with their «fusibility». The term «fusibility» is used here to denote the temperature, to which the glass under question must be heated to impart to it a definite conventional viscosity of about 100 poiseuilles.

Investigation of two component glasses showed that the spectral absorption varies with the polarizing capacity of the cations of the «basic» oxides in the glass as well.

To illustrate this relationship the spectral curves for some of the glasses we investigated, which were coloured by cobalt and uranium compounds, are given

in Figs. 1, 2 and 3. Along the abscissae are plotted wave-lengths, and along the ordinates, spectral absorption computed from the formula

$$E' = \frac{1}{ld}(\lg F_0 - F_\tau)$$

where F_0 is the incident light flux; $F\tau$, the emerging light flux let through by the glass; l, the thickness; d, the specific gravity (density) of the glass.

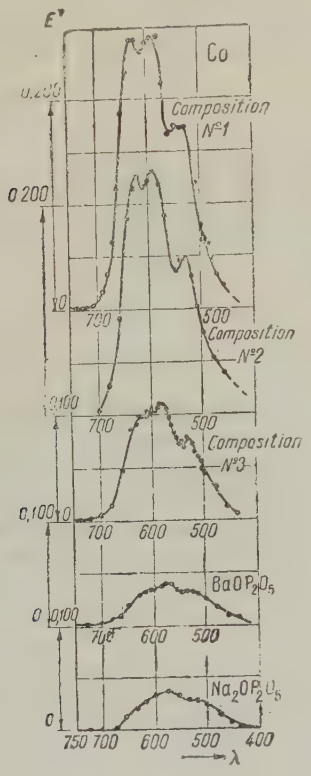

Fig. 1

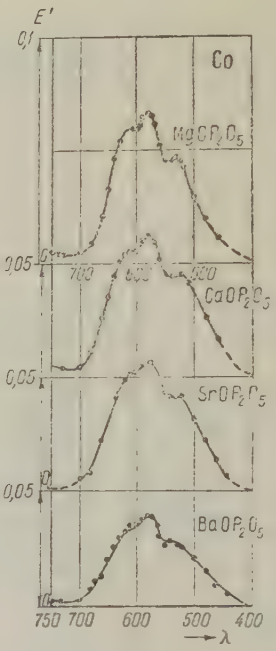

Fig. 2

The curves in Fig. 1 are for glasses coloured by cobalt compounds. The compositions of glasses No. 1, 2 and 3 are given in the accompanying table.

No. of glass	Molecular composition of glass
1	0.06 CaO; 0.45 Al_2O_3; 1.37 SiO_2; 0.18 B_2O_3; 1.00 P_2O_5
2	0.04 BaO; 0.22 Al_2O_3; 0.12 B_2O_3; 1.00 P_2O_5
3	0.26 K_2O; 0.20 Al_2O_3; 0.08 B_2O_3; 0.20 MgO; 1.00 P_2O_5

Among the glasses investigated, the most refractory is that of composition No. 1, and the least refractory, that of the composition $Na_2O \cdot P_2O_5$.

Since all the glasses compared had the same concentration of colouring matter, differences in character of the glasses are due to differences in molecular structure, and changes in the intensities of the absorption bands should be regarded as the result of a shift in the equilibrium between cobalt ions of maximum coordinational saturation and coordinationally unsaturated ions (6).

Fig. 2 shows the spectral curves for «metaphosphates» of the alkaline earths. The glasses are arranged in order of the respective polarizing abilities of the cations $Mg^{\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$. The structures of the spectra change in the same order. The difference in the «fusibility» of the glasses is insignificant, so is the difference in the absorption spectra.

By comparing a large number of spectral curves that have not been included in this brief paper, we have established that the absorption spectra of fusible glasses in which the colouring matter is of constant valency—cobalt, nickel,

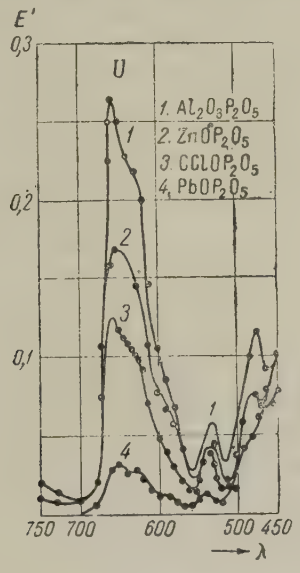

Fig. 3

copper *, are formed primarily by coordinationally saturated compounds of the colouring matter. As the glasses become less fusible, the absorption bands representing the coordinationally unsaturated compounds become more intense. Thus, these differences in the absorption spectra are due to differences in structure. between fusible and refractory glasses.

On the basis of a number of investigations ([7]) it may be assumed that the structural peculiarity of all fusible glasses is an interruption in the stability of their structural bonds, due to the presence of a certain amount of oxygen ions polarized at one end, in other words, to the presence of structural «cavities», arranged statistically throughout the structural lattice of the glass. The peculiarity for refractory glasses is just the opposite.

We assume that in the case of fusible phosphate glasses which are of «friable» structure, the ions of the colouring matter take up positions in the structural «cavities» just like alkaline ions, and interact weakly with the polarized oxygen ions. This accounts for the high coordination number of the ions and for the absorption spectra being analogous or close in structure to the spectra of the hydrated cations of colouring matter. In the case of refractory glasses which are structurally stable, the colouring matter ions wihich now occupy primarily the places of structure forming ions, react more vigorously with the oxygen ions, and this accounts for the lower coordination number and for the absorption spectra being analogous to the spectra of complex anions. Colouring matter of variable valency—manganese, chromium, uranium, iron in phosphate glasses is usually in a low state of oxidation.

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* Copper is included in this group arbitrarily.

The reductive capacity of phosphate glasses increases as their structural stability rises, since the stabler the glasses are structurally, the higher the temperature they require for fusion.

Fig. 3 gives the spectral curves for phosphate glasses coloured by uranium compounds. They are formed by the superposition of the absorption bands of quadri- and hexavalent uranium, the two forms of the colouring matter present in the glass ([8]).

A comparison of the curves shows that the absorption band located in the red part of the spectrum belonging to quadrivalent uranium in solution gradually increases in intensity as we pass from the lead «metaphosphate» to the aluminium «metaphosphate» variety.

A comparison of the two kinds of glasses (phosphate and silicate) shows that the reductive action of the glass base depends also upon the ability of the glass forming ions ($Si^{\cdots\cdot}$, $P^{\cdots\cdot}$) to add on oxygen, and hence the preponderance of colouring matter compounds of low and variable valency is due to the high polarizing capacity of the phosphorous ion.

The State Optical Institute.

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GEOCHEMISTRY

CONTENT OF COPPER, NICKEL, COBALT AND OTHER ELEMENTS OF THE IRON FAMILY IN NATIVE WATERS

By D. P. MALIUGA

(Communicated by A. E. Fersman, Member of the Academy, 24.III.1945)

The content of copper, nickel and cobalt in native surface waters is quite insignificant; like that of many other heavy metals it does not exceed a few millionth sections of a per cent. This is caused by a relatively high pH of river and sea-waters (pH = 8.0) at which heavy metals are not capable to remain in solution, and settle as hydroxides. Different heavy metals are not precipitated at the same rate, however, which leads to a certain equalization of their content in the hydrosphere, preventing the existence of a constant relation between the sediments of different origin.

Although the first indirect evidence on the discovery of copper, nickel and cobalt in sea-waters dates from nearly 100 years ago ([2,3]), information concerning the content of these elements in native surface waters still remained rather scanty ([1]). For example, there was no data as to the content of cobalt in river-waters, while for nickel no more than two determinations were available ([4]).

In the course of our investigation of the geochemical migration of copper, nickel and cobalt in the weathering crust, we had, therefore, to carry out a systematic study of the distribution of these elements in native water, as well as in sediments and sedimentary rocks. For this purpose we have developed a special method for the determination of small amounts of copper, nickel, cobalt and other metals ([5]), the methods commonly applied being found inadequate.

W a t e r A n a l y s i s. Water samples, up to 1 litre capacity, were evaporated in glass retort, the syrup-like residue was neutralized with sulphuric acid, transferred to quartz dishes, evaporated until dry, and heated in an electric muffle at a temperature of 600°C. The ash residue treated in this way was solved in strong hydrochloric acid under addition of 2—3 drops of nitric acid. Upon addition to the diluted solution of rubeanic acid—$H_2NCSSCNH_2$ (diamide-dithio-oxalic acid), citric acid, and alkalinization of the solution with ammonia, copper, nickel and cobalt (zink and cadmium) separated from the rest of metals in the form of sparingly soluble rubeanates. After cobalt had been separated from the acetic acid solution with x-nitroso-β-naphtol, polarograms of copper and nickel (zink and cadmium) and of cobalt were taken separately. The quantity of the metals was estimated from a comparison of the respective polarograms with the standard ones.

As may be seen, our measurements involved water of rivers and lakes of the Russian platform, slightly altered waters of mountain rivulets (Akkura River) and alpine lakes (Kara-Kul Lake), waters of open and closed seas, *etc.* The data obtained on the content of copper, nickel and cobalt in those waters (Table 1),

Table 1

Place of sampling	Quantity of metal discovered, in %			Ratio
	Co	Ni	Cu	Co : Ni : Cu
Volga River, at the town Gorki, upstream	$6.7 \cdot 10^{-7}$	$1.3 \cdot 10^{-6}$	$3.8 \cdot 10^{-6}$	1 : 2 : 5.7
Dnieper River, near the vil. Starosselye	not measured	$6.3 \cdot 10^{-7}$	$1.6 \cdot 10^{-6}$	—
Dnieper River, at the town Lubech	$2.3 \cdot 10^{-7}$	$5.6 \cdot 10^{-7}$	$5.6 \cdot 10^{-7}$	1 : 2.4 : 2.4
Desna River, at the landing place Khatianovka	not measured	$3.6 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	—
Oster River, at the vil. Ivangorod, Chernigov province	$1.9 \cdot 10^{-7}$	$1.9 \cdot 10^{-7}$	$2.3 \cdot 10^{-6}$	1 : 1 : 12
Don River, near the town Rostov, upstream	$5.5 \cdot 10^{-7}$	$5.7 \cdot 10^{-7}$	$1.4 \cdot 10^{-6}$	1 : 1 : 2.5
Moscow River, near the town Zwenigorod, upstream	$8.2 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	$2.2 \cdot 10^{-7}$	1 : 1.5 : 2.7
Kliazma River, near the station Kliazma	$1.9 \cdot 10^{-7}$	$3.9 \cdot 10^{-7}$	$1.0 \cdot 10^{-6}$	1 : 2 : 5.2
Manych River, north of the town Salsk	not measured	$5.3 \cdot 10^{-7}$	$9.0 \cdot 10^{-6}$	—
Kuma River, near the station Mineralnye Vody	» »	$3.9 \cdot 10^{-7}$	$1.0 \cdot 10^{-6}$	—
Ural River, near the town Orsk, upstream	$1.1 \cdot 10^{-7}$	$5.4 \cdot 10^{-7}$	$4.7 \cdot 10^{-7}$	1 : 5 : 4.7
Ob River, near the vil. Bragino	$1.9 \cdot 10^{-6}$	$7.5 \cdot 10^{-6}$	$4.2 \cdot 10^{-6}$	1 : 4 : 2.3
Urov River, at the vil. Talakan	$7.4 \cdot 10^{-8}$	$1.3 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$	1 : 1.8 : 7
Akbura River, near the town Osh, upstream	$1.2 \cdot 10^{-7}$	$1.0 \cdot 10^{-6}$	$4.4 \cdot 10^{-7}$	1 : 8.3 : 3.6
Orlovo Lake, Moscow province	$6.5 \cdot 10^{-7}$	$1.9 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$	1 : 2.9 : 4.8
Vassilievskoe Lake, Moscow province	$5.7 \cdot 10^{-7}$	$1.3 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$	1 : 2.3 : 3.7
Baikal Lake (sampling done at different depths)	$2.3 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	$6.0 \cdot 10^{-7}$	1 : 2.2 : 2.6
Kara-Kul Lake (sampling done in front of the meteorolog. station)	$3.3 \cdot 10^{-8}$	$1.1 \cdot 10^{-7}$	$3.2 \cdot 10^{-7}$	1 : 3 : 10.0
Bolshoe Chussovoe Lake (Urals)	$1.0 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$	$1.8 \cdot 10^{-6}$	1 : 3.2 : 1.8
Maloe Chussovoe Lake	$1.3 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	1 : 2.6 : 0.8
Aral Sea (sample taken from the surface, 5 km from the shore)	$5.4 \cdot 10^{-8}$	$2.6 \cdot 10^{-7}$	$4.6 \cdot 10^{-7}$	1 : 4.8 : 8.5
Barentz Sea (sampling done before entering Yarnysh Bay)	$1.5 \cdot 10^{-7}$	$3.4 \cdot 10^{-7}$	$7.4 \cdot 10^{-7}$	1 : 2.3 : 5
Black Sea, Sebastopol Bay	$4.8 \cdot 10^{-7}$	$7.7 \cdot 10^{-7}$	$1.6 \cdot 10^{-6}$	1 : 1.6 : 3.3
Black Sea, Karadag biolog. station	$2.5 \cdot 10^{-7}$	$5.1 \cdot 10^{-7}$	$1.7 \cdot 10^{-6}$	1 : 2 : 6.3
Black Sea, middle of the sea (sample taken from a depth of 1700 m)	$3.3 \cdot 10^{-7}$	$4.5 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$	1 : 1.4 : 4

as well as literary data available, make it possible to form an idea as to the range of variation and average content of these metals in the most widespread waters of the Earth' surface. Thus, the waters of rivers and fresh-water lakes contain $4.3 \cdot 10^{-7}$ per cent of cobalt, $1.1 \cdot 10^{-6}$ per cent of nickel and $2.0 \cdot 10^{-6}$ per cent of copper. For the sea-waters the respective figures are $2.1 \cdot 10^{-7}$, $3.4 \cdot 10^{-6}$ and $4.1 \cdot 10^{-6}$. We thus see that, unlike the relation between the mean contents of cobalt, nickel and copper recorded for soils (1 : 4 : 2) ([6]) and for rocks (1 : 10 : 5), the respective relation in river-waters makes up 1 : 2.5 : 4, while in sea-waters it is 1 : 1.6 : 20. Here we observe a pronounced tendency of cobalt, and especially of copper, to concentrate in the hydrosphere, which is very interesting from the geochemical point of view.

Certain continental basins located in biogeochemical provinces ([6]) rich in nickel and cobalt (as, for instance, the Urals) show a rather high content of nickel and cobalt in their waters (lakes Bolshoe and Maloe Chussovoe, for example). On the other hand, the low content of these metals in the waters of the Aral Sea, Lake Kara-Kul, is in full agreement with their location in a desert zone, poor in these metals. The content of cobalt, nickel and copper in the waters of the Russian platform holds an intermediate place, which may be accounted for by the rather peculiar conditions of the formation of their salt residue, which proceeded mainly by way of leaching-out by meteoric waters of the soils of the platform, whose content of heavy metals is also a medium one.

There is also observed a relative concentration of copper, nickel and cobalt in the brown waters of peat lakes, Vassilievskoe and Orlovo. This case coincides with the generally observed phenomenon of accumulation of elements of the iron family in waters of this kind, which are high in organic substances and products of their decomposition. It is also in good agreement with the natural migration of heavy metals from soils and rocks of land and sea in the form of oxides and protoxides of humates, bicarbonates, *etc.* However, the mixing up of river-waters with sea-waters of higher salinity is known to create favourable conditions for the precipitation from solution of hydroxides of iron, manganese and aluminium. Analyses of deposits of this kind, which are known by the name of muds have revealed an invariable presence of vanadium, nickel, copper, cobalt and other «minor» elements of the iron family. The unstable ratios at which these metals occur in riverine, marine and other deposits testify to their different reaction to the physical-chemical and biochemical phenomena that take place in the hydrosphere (Table 2).

Table 2

Kind of deposits, *etc.*	Average content of metals, in %						Ratio Co : Ni : Cu : V : Fe : Mn
	Co	Ni	Cu	V	Fe	Mn	
River-delta silts*	$3.7 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$3.5 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$	5.14	$8{,}0 \cdot 10^{-2}$	1 : 3 : 1 : 4.3 : : 1400 : 20
Sea deposits* . .	$2.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-2}$	$8.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-2}$	5.6	$3.4 \cdot 10^{-1}$	1 : 10 : 3.2 : 8 : : 2200 : 140
Iron-manganese concretion (marine)**	$2.0 \cdot 10^{-1}$	$7{,}7 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$	$4.6 \cdot 10^{-2}$	19.5	12.8	1 : 3.8 : 1.4 : : 0.2 : 97 : 64
Native waters (sea) according to data by Vinogradov and by the present author	$2.1 \cdot 10^{-7}$	$3.4 \cdot 10^{-7}$	$4.1 \cdot 10^{-6}$	$5.0 \cdot 10^{-8}$	$5.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-7}$	1 : 1.6 : 20 : : 0.24 : 24 : 2

* According to F. W. Clarke ([7]) and the present author's data.
** According to R. Irvine and J. Gibson ([8]).

Thus, in deltaic muds, formed by way of a purely mechanical deposition of rather coarse clastic material of rocks and minerals (field spar, quartz, *etc.*), the ratio of cobalt to nickel, copper and vanadium is 1 : 3 : 1 : 4.3; whereas in terrigenic and other sea-muds, which are largely formed by way of physical-chemical deposition of hydroxides of metals, the ratio observed is 1 : 10 : 3.2 : 8. The respective values for iron manganese concretions (sea) are 1 : 3. 8 : 1.4 : 0.2. Keeping in mind the ratio of cobalt to nickel, copper and vanadium in riverine waters, *viz.* 1 : 2.5 : 4 *, and in sea-waters, 1 : 1.6 : 20 : 0.24, we have to state that the settling of these metals from solution proceeds at a rate which does by no means correspond to their respective content in native waters. Thus, nickel and vanadium settle mostly within the littoral zone (co-deposition with iron, manganese and aluminium). The separation of copper and cobalt proceeds at a markedly lower rate, which leads ultimately to a relatively higher content of these metals in the hydrosphere **.

The historical process of the formation of deposits in the hydrosphere goes on continuously up to the present day. In young sedimentary rocks we do not infrequently meet with deposits similar to the most ancient ones; we determine their origin by the content and ratio of chemical elements, and so on.

In this way we attempt to shed light upon the genesis of certain «mute» series of the stratisphere, which had been formed also under a continuous action of the native surface waters, and whose chemical composition underwent no essential alterations in the course of geological time.

The W. I. Vernadsky
Laboratory of Geochemical Problems.
Academy of Sciences of the USSR.

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* No data as to the content of vanadium in riverine waters are available.

** Differences in the behaviour of copper, nickel and cobalt in the process of their co-deposition with hydroxides of iron, aluminium and manganese can be observed in the case of artificial mixing of riverine and marine waters. In our corresponding experiment the deposit thus obtained was found to contain 61 per cent of cobalt, 97.6 per cent of nickel, and 12.5 per cent of copper.

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BIOCHEMISTRY

ON THE REDUCTION OF ORTHO-DINITROBENZENE IN GREEN PLANTS

ON THE THEORY OF REGULATION OF PROTEIN EXCHANGE IN PLANTS

By A. A. GUREWITSCH

(Communicated by A. N. Bach, Member of the Academy, 8.IX.1944)

In our previous note ([1]) it has been shown that our experiments on the reduction of *o*-dinitrobenzene in plants give an idea of the redox conditions that prevail in green leaves, both in the dark and when exposed to light. As a result, a definite conclusion can be drawn with regard to the theory of regulation of protein metabolism in plants, which has been advanced by Mothes ([2,3]).

As well-known, the main agent responsible for whether the protein substances in plants will serve for synthesis, or will undergo decomposition, is their intracellular redox potential; under natural conditions the value of the latter is largely determined by the concentration of free oxygen in the cells. If the oxidation potential is high, there is synthesis of protein substances, whereas at a low value of the oxidation potential, a hydrolytic breakdown of proteins into aminoacids takes place.

This relation between the biochemical process which is of no redox nature by itself, and the redox potential should be accounted for by the influence of the latter upon the state of intracellular proteolytic enzymes. Such enzymes are the papainases whose effect is not manifest unless specific activizers are present in the cell in the form of glutathione and other compounds with sulphohydryl radicals (—SH). These compounds are stable only in the case of a low redox potential; as the latter increases, they are oxidized, suffering dehydration, and pass into the sulphide form (—S—S—), losing their power to activize the papainases which pass therefore into a resting state, owing to which the hydrolysis of proteinic substances is arrested.

According to Mothes' interpretation, synthesis and hydrolysis of proteinic substances proceed in the cell simultaneously; if so, their synthesis or breakdown should be due to a mere prevalence of the one of these two opposite processes. In the case of low oxidation potential, at which papainases are activized and proteolysis proceeds at a higher rate, a breakdown of proteins takes place, while at a high value of the oxidation potential, leading to an arrest of proteolysis, the inverse phenomenon, *viz.* synthesis of proteins, is observed. Mothes supposes, however, without developing this assumption at any length, it is true, that the oxidizing potential affects not only the hydrolysis, but also the synthesis of proteinic substances of the cell, the synthesis being slowed down as the oxidizing potential decreases.

On the basis of his conceptions referred to above, Mothes suggests an interpretation of the effect of light upon the protein exchange in green leaves; under

natural conditions this effect is expressed in the 24-hour periodicity of the transformations of proteinic substances: in leaves exposed to light, a synthesis of protein substances takes place, whereas in the dark these substances undergo decomposition ([4]).

Mothes is thus led to conclude that this relation is due to the effect produced by light upon the intracellular oxidation potential of the leaf. This assumption of his has been based upon the fact that *in* green leaves a high oxidation potential is prevalent, whereas in the dark it is low. The interpretation he gives to this phenomenon is that in leaves exposed to light oxygen concentration is increased, owing to its formation in the course of photosynthesis and to the free diffusion through the open stomata. Contrary to this, in the dark the concentration of oxygen decreases as a result of an absence of photosynthesis, of closed stomata, and also because of the absorption of oxygen by respiration.

We thus see that the existence of the relation here discussed between the light and the redox potential in the green leaf is adopted by Mothes from purely indirect evidence rather than from experimental data, in spite of the fact that the interpretation this writer gives to the regulation of protein exchange in green leaves is essentially based upon this very statement.

Our experiments described in an earlier paper ([1]), dealing with the reduction of *o*-dinitrobenzene in the leaves of wheat and *Elodea*, enable us to make a definite conclusion as to the relative values of the redox potentials in the green leaves when withheld from light or exposed to the latter.

These experiments went to demonstrate that in the dark, under a free access of oxygen of the air to the portions of leaves immersed into dinitrobenzene solution, the leaf shows a high oxidation potential, at which no reduction of *o*-dinitrobenzene takes place. It is not until the access of air is impeded by fully immersing the leaves into dinitrobenzene solution and withholding them from light, that the oxidation potential drops so low as to lead to a reduction of ortho-dinitrobenzene.

In our experiments carried out under liberal aeration, not only a considerable part of the leaf's surface, but also the surface of the cut were brought into contact with air; in this way oxygen was allowed to penetrate into the leaf not only through its epidermis, but through the surface of the section directly into the intercellular spaces. In order to prevent the latter circumstance and create aeration conditions approaching those prevailing in nature, we carried out experiments in the dark with young wheat leaves, in which the surface of the cuts was covered with paraffin. Otherwise these experiments did not differ from those earlier described. Under these conditions no aeration of the leaf could take place unless by diffusion of oxygen through the cuticle, the stomata being closed in the dark, as shown by subsequent testing of their condition by the infiltration method ([5] p. 88).

In control experiments with decreased aeration, wheat leaves were not entirely immersed into dinitrobenzene solution, as it was done in our earlier corresponding experiments. In order to prevent the possible direct supply of dinitrobenzene through the surface of the cut, which would lead to conditions incomparable with those prevailing in the main experiments, reduced aeration was provided by covering with paraffin the whole leaf surface, instead of the surface of the cut alone. The experiment lasted 24 hours, temperature being kept at 15—17° C.

The results obtained went fully to confirm the data of our corresponding experiments, carried out under similar conditions save for the procedure of paraffin covering ([1]). In the dark, under conditions of full aeration, there was no reduction of *o*-dinitrobenzene by wheat leaves. The solution remained colourless and showed no reaction either for *o*-nitro-phenylhydroxylamine or *o*-nitraniline.

Unlike this, in the control experiment which was carried out under conditions of impeded air supply, there was intense reduction of *o*-dinitrobenzene. The solu-

tion was found to assume a yellow colour and displayed the presence of *o*-nitrophenylhydroxylamine and *o*-nitraniline.

In order to satisfy myself that the leaves in the main experiment have not lost their viability, and to demonstrate at the same time that *o*-dinitrobenzene did actually suffer no transformation in this experiment, the experiment was repeated with the same leaves and solution, according to the scheme of the control experiment involving decreased air supply. With this aim in view the leaves used for the main experiment were somewhat curtailed at their basal part, and the cut, as well as the whole surface of the leaf which comes into contact with the air, were covered with paraffin. This made, the leaves were immersed with their apical parts into the same *o*-dinitrobenzene solution as had been used for the main experiment, and so kept in the dark at the same temperature for another 24 hours. The results were in full conformity with the results of the control experiment: the solution assumed a yellow colour and showed a reaction for *o*-nitrophenylhydroxylamine and *o*-nitraniline.

Our experiments thus went to demonstrate that in the dark, under aeration conditions most closely approaching the natural ones, the oxidation potential in wheat leaves is so high that *o*-dinitrobenzene does not undergo reduction in them.

This should be taken to mean that the oxygen of the air is allowed to diffuse into the leaf directly through its cuticle, at a rate sufficient to satisfy the requirement in oxygen of the breathing cells. We thus see that Mothes' assumption to the effect that the oxidation potential of green leaves suffers a considerable drop in the dark, finds no experimental support.

The results of our experiments involving the reduction of *o*-dinitrobenzene by green leaves exposed to light, also fail to confirm Mothes' theory of the redox potential as a regulator of protein metabolism in plants. According to this theory, in green leaves exposed to light, and especially in the chloroplasts of the assimilating cells, in particular, a high oxidation potential is prevalent, which is due not only to a free access of oxygen through the open stomata, but also to the formation of oxygen in the green plastids in the process of photosynthesis. Mothes makes this fact accountable for the protein synthesis taking place in green leaves exposed to light, being concentrated chiefly in the chloroplasts, as has already been pointed out by various writers ([6,7]).

On the other hand, our earlier experiments ([1]) have shown that in the leaves of wheat and *Elodea* *o*-dinitrobenzene undergoes intense reduction. This testifies to the fact that the oxidation potential is very low in green leaves exposed to light.

However, this is true of the chloroplasts only, whose activity is directly responsible for the reduction of *o*-dinitrobenzene in the green leaves in the light, as has been shown by our earlier experiments. The oxidation potential of the colourless protoplasm of green cells exposed to light has probably a much higher value than that of chloroplasts. This cannot be revealed with the aid of *o*-dinitrobenzene as an indicator, since, as has already been shown in ([1]), its reduction is an irreversible reaction.

We are thus brought to conclude that the real relation between the values of the redox potentials in green leaves when exposed to light or kept in the dark is, as a matter of fact, the opposite of what Mothes takes for granted in his theory of regulation of protein exchange in plants.

Bearing out the lack of sound foundation of the principal statement of Mothes' theory of the oxidation potential as a regulator of protein metabolism in plants, the results of our experiments are in full agreement with those obtained by Paech ([8, 9]) on the basis of other experimental data. It should be pointed out that, although disposing of no experimental data bearing upon the redox potentials in the green leaf, Paech has nevertheless arrived at a correct conclusion. «It cannot be asserted *a priori*», he says, «that during assimilation an especially high oxidation potential prevails in the chloroplasts, since the process of assimilation belongs among the most intense reduction processes which the plant

is capable to undergo. The fact that the oxidation potential in the rest of the plasm may be raised under the influence of oxygen freed in the process of assimilations, is still to be proved» ([9]).

The results of our experiment are also in fair agreement with the corresponding data by Rapkine and Wurmser ([10]); according to these writers, the indophenols which undergo oxidation when exposed to the air, are reduced in the protoplasm of the cells of *Spirogyra*, in spite of the fact that when exposed to light, these cells give place to the liberation of oxygen.

Laboratory of Plant Physiology and Microbiology.
The K. A. Timiriazev Agricultural Academy.
Moscow.

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GEOLOGY

A STRUCTURAL CLASSIFICATION OF ELUVIUM

By L. G. POSPELOV

(Communicated by V. A. Obruchev, Member of the Academy, 26. XI. 1944)

By eluvium, according to the classical definition, are meant the products of weathering of rocks lying in the place of their original formation. In practice, however, the prospector often describes as eluvium products that have suffered considerable shifting in the process of their formation.

To settle the questions arising in the practice of structural analysis of an ore-field covered with considerable overburden and in the practice of searching for deposits of eluvial clays, the present author undertook detailed explorations of the eluvial-diluvial deposits of the Salair bald mountain. Here the process of a detailed structural survey of the field of development of the Salair polymetallic deposits (Kemerov district of West-Siberia) was accompanied by sinking a great many test-pits (over 3000 test-pits and holes within an area of 3.5 sq. km.), carried out for the «Zvetmetrazvedka», and was based on large-scale quarrying, which permitted numerous special observations and correlations to be made. These explorations have shown that the gravitational flow of weathered rocks may extend over a large distance—up to a hundred metres and more, without disturbing the geological boundaries between the masses flowing down the slope, which may therefore for a long time retain their characteristic structural features. A very regular structural gradation of the different phases of formation of eluvium was thus revealed, and this applies also to other regions of Siberia where the author worked. So the phenomenon is of a general nature and its great practical value for prospecting is obvious. Leaving a more detailed discussion and illustration to a special paper, the author thinks it useful for the present to make the following preliminary communication.

If in the process of formation of the weathering crust not the location but the structural features of the eluvial masses are preserved, inherited from the original deposits of country rocks, it is only natural to lay at the base of a morphological classification of the products of weathering not the degree of their shifting, but the degree of preservation of the structural elements of mountain masses in the process of their translocation by gravity in the weathering crust.

Therefore we use the name of e l u v i u m to describe physically disintegrated or chemically altered rocks, which have preserved the relict structural features of the mass of the initial rocks and have retained continuity of transition to the original country rocks.

Accordingly, the name of d i l u v i u m is applied to physically disintegrated or chemically altered rocks, intermixed and therefore retaining neither their

initial structural features nor continuity of transition to the original rocks, but having acquired gradations to formations redeposited by water and wind.

Since the disintegration and chemical alteration of rocks result in their yielding to the force of gravity, a gravitational flow of weathered rocks is produced; the structure of the mass of these rocks undergoes a succession of changes, which may be considered to form a structural-genetic series (Fig. 1).

1. Structural Eluvium, an eluvium, in which not only the boundaries of the original rock with the adjacent ones have been preserved, but also

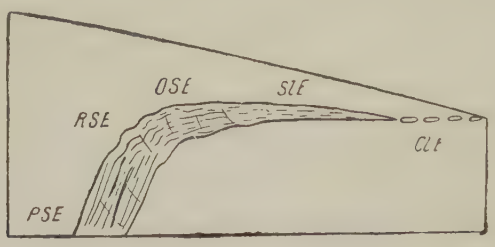

Fig. 1. Scheme of classification of eluvium. *PSE*, primary structural eluvium; *RSE*, rolled-up structural eluvium; *OSE*, overturned structural eluvium; *SlE*, structureless eluvium; *ClD*, closed diluvium

its structural features: characteristic fracturing, schistosity, system of veinlets, outlines of clayey minerals, *etc*.

Structural eluvium falls into:

a) Primary, an eluvium *in situ*, retaining the original mode of occurrence.

b) Rolled up («rolled-up heads»), an eluvium rolled up in the direction of slope: the structural features have been preserved, but the original mode of occurrence has been disturbed, new structures appearing as, for instance, contorsion folding of the rolled-up deposits.

c) Overturned, an eluvium flowing down the slope, but still retaining some characteristic features of the mass of original rocks, gradually disfigured by the newly formed flow structures: for the Salair bald mountain it has been established that an overturned structural eluvium is locally encountered some dozens of metres away down the slope from the primary eluvium of the same rock.

2. Structureless Eluvium, an eluvium in which in the main only the boundaries of the original rock with the other rocks have been preserved, as well as only some internal structural characters, such as, *e. g.*, traces of schistosity, or on the contrary, evidence of the primary massive character of the rocks, relict remains of quartz veinlets ground up in the course of gravitational flow, *etc*. Prevalent are, however, various structures due to gravitational flow or to a building process in which vertical sinking actively participated, for instance, a vigorous leaching or suffusion (projected eluvium).

For the Salair mountain it has been established that the structureless eluvium flowing down the slope occurs within a distance of up to 150 m from the primary eluvium of the same rock, retaining the distinctness of geological boundaries of the different rocks between one another.

For want of space, no detailed discussion of structureless eluvium will be given here.

Diluvium may be subdivided into two main genetic types.

1. Closed diluvium, an eluvium of different rocks disintegrated and mixed as a result of a subsoil gravitational flow. Gravitational flow structures are predominant. In the upper horizons there appears evidence of aqueous and aeolian grading, wind and water taking part in the shifting of material.

2. Open diluvium, a diluvium formed by disintegration of primary eluvium exposed at the surface.

The structural-genetic series of eluvium-diluvium given above characterizes chiefly the processes of gravitational flow of weathered rocks down the slope. The members of this series have a different development in different flows; some of them fall out altogether. But the less stony the overburden, the more complete the development of the given genetic series.

Considerable originality is introduced into the given classification by a vertical gravitational flow developed at the places of an intensive supply of material to the surface by underground waters.

In this respect a particular part in the Salair is played by near-contact karst. By this term is meant the karst developed in limestones at their contact with silicate rocks. Its peculiarity lies in the fact that it forms cavities, thus giving rise to an eluvial caving-in of the adjacent silicate rocks, with the ultimate formation of various forms of structureless eluvium. If the thickness of the silicate rocks is rather great, all the transitions from the caved-in to the primary eluvium may be traced (Fig. 2,*а*). If the silicate rocks form a small layer or stock in limestones, the sagging and caving-in may affect the whole mass of the silicate rock, of which the primary eluvium may be discovered only in some deep horizons or in selectively preserved areas (Figs. 2,*б* and *в*). Karst phenomena may so much distort the relict structures of the mass of the original rocks, that very careful search is necessary to detect their presence. Therefore in such cases it is very easy to mistake a near-contact karst for common one.

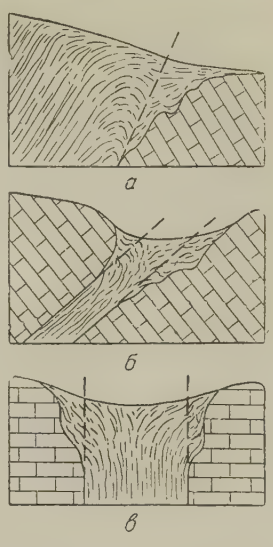

Fig. 2. Near-contact karst. Dotted lines show primary geological boundaries between the silicate rock and the limestones

The deciphering of such cases permitted many fire-clay deposits in the Salair to be transferred from «karst» deposits, with which they had been previously classed, to normal eluvial deposits. This was of great value because prospecting for eluvial deposits here could be conducted by a structural method similar to the method used by the author in the search for polymetallic deposits in the Salair, which will be described elsewhere.

West-Siberian Branch
of the Academy of Sciences of the USSR.
Novosibirsk.

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GEOLOGY

SOME NEW SPECIES OF SMALL FORAMINIFERS FROM THE TOURNAISIAN OF THE ISHIMBAYEVO OIL-BEARING REGION

By I. S. SULEIMANOV

(Communicated by P. I. Stepanov, Member of the Academy, 26.VIII.1944)

All the spherical forms from the Tournaisian of the Ishimbayevo region, discovered by the present author, have been subdivided by him into two groups. The first group comprises forms with a smooth surface without distinct apertures: to the second are referred forms with numerous apertures. As to their external appearance, the forms belonging to the first group resemble the representatives of the genus *Psammosphaera*. The wall of the latter consists, however, of a thin layer of pseudochitin, having an external coating of well-cemented sand particles, small fragments of mica, spicules of sponges, or shells of other foraminifers. Unlike this, in the forms here described it consists of very fine calcite grains without any inclusions of foreing particles. On account of the great importance of this distinctive feature, the spherical forms of the first group have been separated out into an independent genus, *Archaesphaera* gen. nov.

The second group of spherical forms differs from the first one by distinctly pronounced and numerous apertures located on the papilliform protuberances of the surface of the shell. Similar forms have at different times been described by various authors who referred them to the genus *Thurammina* (1). As may be seen from literature, the wall in *Thurammina* consists of small, well-cemented sand particles, while the forms from the Etroeungt beds have a different structure of the wall, consisting of minute calcite grains, sometimes showing striation in the middle of the theca. For this reason monothalamic forms with numerous apertures and a uniform calcareous wall have been separated out into a special genus under the name of *Parathurammina* gen. nov.

The *Parathurammina* and *Archaeosphaera* from the Palaeozoic of this country are studied for the first time, and therefore their occurrence in a definite horizon of the Tournaisian deposits and in the Etroeungt beds gives as yet no possibility to speak of their significance as reliable guide fossils. But the very fact of their discovery in the same deposits of the Ishimbayevo and Tuymaza regions makes us assume that they are characteristic of these deposits in the near-Ural area.

The major part of the materials which served us for the description of these foraminifers, was obtained from cores of drill-wells of the Ishimbayevo region; the material from one well of the Tuymaza region (well 20) has been used to a much smaller extent.

As a result of a study of the vertical range of small foraminifers, it has been possible to subdivide the Tournaisian stage into a number of horizons, a brief characteristic of which is given below.

Table 1

Distribution of New Forms and Some Old Forms in the Tournaisian Deposits of the Ishimbayevo Region

Species	Horizons			
	$C_1^{étr}$	$C_1^{t_1}$	$C_1^{t_2}$	$C_1^{t_3}$
Parathurammina dagmarae sp. nov.				Absence of deposits (erosion)
P. oldae sp. nov.				
P. cuchmani sp. nov.				
Archaesphaera minima sp. nov.				
A. magna sp. nov.				
Spiroplectammina chernyshinensis Lip.				
Endothyra glomiformis Lip.				

$C_1^{étr}$—Etroeungt beds represented by dolomitized limestones and dolomites, with stylolite seams filled with greenish-grey clay, with a complex of foraminifers: *Parathurammina dagmarae* sp. nov., *P. oldae* sp. nov., *P. cuchmani* sp. nov., *Archaesphaera minima* sp. nov., *A. magna* sp. nov. Thickness 32—35 m. These layers are separated out on the basis of data of a correlation with the section of the Tuymaza region, where *Parathuramminae* are found together with *Endohyra communis*, the guiding significance of which for the Etroeungt beds has been established by Rauzer-Chernoussova (2).

$C_1^{t_1}$—limestones and dolomites, with karst phenomena, with stylolite seams filled with greenish-grey clay, with foraminifers: *Archaesphaera minima* sp. nov., *A. magna* sp. nov., *Bathysiphon bashkiricus* sp. nov., *Nodosaria* (?) sp. Thickness 38—39 m. This horizon is separated out as an intermediate one from the complex of small foraminifers between the Etroeungt beds and the horizon, of which the microfauna of the Chernyshino beds of the Moscow basin is characteristic.

Table 2

Correlation of Sections of the Tournaisian Deposits in the Ishimbayevo and the Tuymaza Regions

Horizons	Ishimbayevo region	Tuymaza region, after A. J. Vissarionova
$C_1^{t_3}$	Eroded	Algal limestones with *Endothyra glomiformis* Lip., *Spirillina plana* Moell, *etc.* Thickness 26—30 m
$C_1^{t_2}$	Organogenous limestones with *Spiroplectammina chernyshinensis* Lip., *Endothyra glomiformis* Lip., *etc.* Thickness 15 m	Organogenous limestones with *Spiroplectammina chernyshinensis* Lip., *Endothyra glomiformis* Lip., *etc.* Thickness 23-28 m
$C_1^{t_1}$	Dolomitized limestones and dolomites with *Archaesphaera minima* sp. nov., *A. magna* sp. nov., *etc.* Thickness 39 m	Dolomitized limestones with *Archaesphaera minima* sp. nov., *A. magna* sp. nov., *etc.* Thickness 17-19 m
$C_1^{étr}$	Dolomitized limestones and dolomites with *Parathurammina dagmarae* sp. nov., *P. cuchmani* sp. nov., *etc.* Thickness 35 m	Limestones with *Endothyra communis* Raus., *Endothyra primaeva* Raus., *Parathurammina cuchmani* sp. nov., *etc.* Thickness 41 m

$C_1^{t_2}$—organogenous limestones with bands of dolomites with *Spiroplectammina chernyshinensis* Lip., *Endothyra glomiformis* Lip., *E. rjausakensis* Tschern., *E. spinosa* Tschern. No small forms characteristic of the underlying beds have

been discovered. Thickness 15 m. According to the complex of microfauna it contains, this horizon is correlated to the Chernyshino beds of the Moscow basin and the analogous deposits of the Tuymaza region.

The section of the Tournaisian deposits of the Ishimbayevo differs from the section of the Tuymaza region by the absence of deposits of the C_1^{1a} horizon. The absence of a whole horizon from the section of the Tournaisian deposits of the region described may be explained either by the erosion of the deposits, or by a break in the accumulation of sediments in the Upper Tournaisian time. The former assumption seems to be more probable, since in the Tuymaza region, according to the data of A. J. Vissarionova, the section of Tournaisian deposits is also considered to be incomplete, and its upper portion has been destroyed by erosion.

Family *Saccamminidae*. Genus *Archaesphaera* gen. nov.

Generic diagnosis: shell free, unattached, globular, with a smooth surface. Wall of shell thin, calcareous, dark, uniform, finely granular. No aperture observed.

Genotype — *Archaesphaera minima* gen. et sp. nov.

Archaesphaera minima sp. nov. Shell minute, free, unattached, globular. Surface of shell smooth. Diameter varies from 0.083 to 0.15 mm. Wall very thin, dark, uniform, consisting of minute calcite grains. No pores in the wall observed. Thickness of wall 0.006 to 0.012 mm. No aperture observed.

Occurrence and age: found in Lower Tournaisian limestones and in the Etroeungt beds of the sections of wells of the Tra-Tau area and at Tuymaza.

Archaesphaera magna sp. nov. Shell globular, free, unattached, with a smooth surface. Diameter of shell 0.26—0.34 mm. Wall thin, dark, uniform, consisting of minute calcite grains. Thickness 0.012 mm. No aperture observed. Comparison: the present form is distinguished from *Archaesphaera minima* sp. nov. by a larger diameter of the shell.

Occurrence and age: same as for the above-described form, with the only difference that this form is encountered in a small number of specimens.

Genus *Parathurammina* gen. nov.

Diagnosis: Shell globular, free, monothalamic. At surface is covered by numerous papilliform protuberances. Wall calcareous, non-agglutinated, sometimes with striae in the middle theca. Apertures numerous on the ends of papilliform protuberances, sometimes faintly pronounced.

Genoholotype *Parathurammina dagmarae* sp. et gen. nov.

Parathurammina dagmarae sp. nov. Shell small, globular, free, non-attached, monothalamic. Surface of shell smooth, covered with numerous papilliform protuberances. Wall thin, dark, calcareous, consisting of fine-grained calcite, sometimes striated. No agglutinated particles have been discovered. Diameter of shell varying from 0.2 to 0.45 mm. Thickness of wall uniform, 0.006—0.012 mm. A certain thinning of the theca observed near the papilliform protuberances. Apertures numerous, rounded, located on the ends of the papilliform protuberances on the surface of the shell. Height of these protuberances 0.06 mm; diameter, 0.006—0.009 mm. Comparison: the form described is distinguished from the representatives of the genus *Thurammina* by the composition of the wall of it shell. From *Parathurammina oldae* sp. nov. it is distinguished by a larger diameter, a somewhat thicker wall and a globular shape of the shell.

Occurrence and age: occurs in large quantities in the Etroeungt beds in the section of the walls in the Tra-Tau area. Not found in the deposits of the overlying beds of the Tournaisian stage.

Parathurammina oldae sp. nov. Shell small, monothalamic, free, unattached, somewhat flattened. Surface of shell smooth covered with numerous papilliform protuberances. Wall dark, uniform, consisting of fine-grained calcite. Shell small. The diameter of the elongated side of the shell varies from 0.26 to 0.32 mm. The diameter of the shorter one, from 0.20 to 0.24 mm. The thickness of the wall is 0.006—0.009 mm. The apertures numerous, situated on the points of the papilliform protuberances of the surface. Comparison: from the above-described *Para-*

thurammina dagmarae sp. nov. this form is distinguished by the shape of the shell and its comparatively small diameter.

Occurrence and age: it is found along with *Parathurammina dagmarae* sp. nov. in some layers of the Etroeungt deposits in the sections of wells in the Tra-Tau prospecting area.

Parathurammina cuchmani sp. nov. Shell almost globular, free, monothalamic. The diameters are comparatively large, varying from 0.38 to 0.48 mm.

Fig. 1. *Archaesphaera minima* sp. nov. Holotype. Well No. 20 (Tuymaza), depth 1203.6 — 1216.5 m, specimen No. 37115, × 80

Fig. 2. *Archaesphaera magna* sp. nov. Holotype. Well No. 3/13 (Tra-Tau), depth 1356.5—1400 m, specimen No. 59601, × 80

Fig. 3. *Parathurammina dagmarae* sp. nov. Holotype. Well No. 3/13 (Tra-Tau), depth 1422.9 — 1427 m, specimen No. 60203, × 80

Wall of shell dark, comparatively thick, consisting of minute calcite grains. Sometimes inclusions of larger crystals of calcite are noted. The thickness of the wall is not uniform. The average value is 0.025—0.038 mm, sometimes reaching

Fig. 4. *Parathurammina oldae* sp. nov. Holotype. Well No. 3/13 (Tra-Tau), depth 1430.8—1433.8 m, specimen No. 60402, × 80

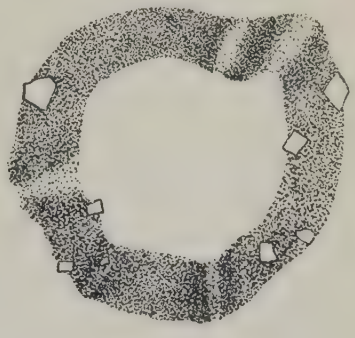

Fig. 5. *Parathurammina cuchmani* sp. nov. Holotype. Well No. 20 (Tuymaza), depth 1216.5—1225 m, specimen No. 37202, × 80

0.051 mm. Apertures numerous, often poorly developed, located on low papilliform protuberances on the surface of the shell. Comparison: from the two forms described above (*Parathurammina dagmarae* sp. nov., *P. oldae* sp. nov.) this form differs sharply in its external shape, comparatively large diameter, thick wall and not always well-pronounced aperture.

Occurrence and age: it is found together with the other *Parathuramminae* in the Etroeungt beds in the sections of the wells in the Tra-Tau prospecting area, and in well No. 20 of the Tuymaza region.

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MINERALOGY

AMPANGABEITE FROM THE YELISSEYEVKA DEPOSIT (UKRAINIAN SSR)

By G. P. BARSANOV

(Communicated by A. E. Fersman, Member of the Academy, 1.X.1944)

Among the minerals of the Yelisseyevka pegmatite deposit investigated in 1938 by N. V. Stal, geologist, who studied the material at the A. P. Karpinsky Geological Museum of the Academy of Sciences of the USSR, she discovered for the first time a mineral belonging to the group of niobotantalates. Upon examination it was found to be an isotropic mineral comparatively rich in uranium; according to its external properties and peculiarities of structure and composition, it was named betafite. Later on, different investigators who continued the work at the Yelisseyevsky deposit, mentioned this mineral as betafite, blomstrandite, or a «mineral unknown». Under these names the specimens were recently studied by the X-ray and chemical methods at the Laboratory of the Institute of Geological Sciences by I. B. Borovsky; however, no detailed mineralogical investigation of this mineral is available. A careful examination of the specimens from the collection of N.V.Stal (collection No. 2917) and a mineralogical and microchemical investigation of this mineral carried out by the present author showed, however, that it does not fit either in external appearance or in composition within the group of cubic uranium-bearing niobotantalates—betafite, blomstrandite or samiresite, described from the island of Madagascar by A. Lacroix ([2,4]), but corresponds most closely to ampangabeite also described from Madagascar.

Pegmatites, containing ampangabeite, are found in the Ukrainian SSR, in the Dniepropetrovsk region, Berdyansk district, near the villages of Novo-Yelisseyevka and Dolinskoye with a number of thick pegmatite veins well-known for large crystals and accumulations of columbite, which was the object of prospecting work. The main ampangabeite occurrences are veins Nos. 4 and 1.

Ampangabeite in the Yelisseyevka pegmatites occurs in strongly crushed and albitized feldspar-muscovite pegmatites, in a characteristic intergrowth and paragenesis with columbite, which was particularly emphasized by Lacroix for Madagascar. The type of pegmatite, according to the classification of A. E. Fersman ([3]), closely corresponds in paragenesis to the III complex type (with a development of geophases C—D), *i. e.* to the same type to which he refers the pegmatites of Madagascar. In the paragenesis of the pegmatites of the Yelisseyevka represented by the chief minerals—microcline-perthite, oligoclase, albite (saccharoidal and lamellar), quartz, muscovite (two generations), spessartite, beryl, apatite, gahnite, columbite, cyrtolite, ampangabeite, euxenite, bismuthinite, basobismutite (?), there are many features in common with the pegmatite

of Ampangabé and Ambatofotsikely on Madagascar, described by Lacroix [4] and Sabot [6], with characteristic columbites quite similar to those of the Yelisseyevka deposit. A characteristic intergrowth of ampangabeite with columbite, the presence of gahnite (as a contact, secondary mineral after Lacroix), and of bismuth minerals. On Madagascar, however, an intergrowth of ampangabeite with euxenite is characteristic, as well as a considerable development of other niobotantalates—ilmenorutile, monazite, *etc.*, which have been discovered by P. Getzeva in the Yelisseyevka deposit. As to betafite and blomstrandite, their paragenesis on Madagascar [2,4], is caracterized by a group of minerals—pink quartz, blue beryl, black, green and polychromous tourmaline, almandine, microcline, lepidolite,—and hence the type of pegmatite, too, is quite different from that in the Yelisseyevka deposit.

Previous to a description of ampangabeite from the Yelisseyevka deposit, the characteristics of the ampangabeite from Madagascar, the only one described in literature, should be briefly reminded. The mineral was first discovered and described by A. Lacroix and analysed by G. Pisani in 1912 [3] from the Ampangabé deposit and later on also from the pegmatites of Ambatofotsikely. According to a number of investigations it was considered to be an altered yttrotantalite (samarskite), which view was expressed in the description of Prior [5]. In his later papers, however, Lacroix [4] on the basis of his own investigations, as well as on the work of Sabot and Duparc [6] and Ungemach [7], insisted upon considering ampangabeite as an independent mineral species, pointing out a certain variability in colour, specific gravity and composition, and referred the mineral to a species closely resembling euxenite. This was also pointed out by Sabot who considered it to be a kind of hydrated euxe-

Mineral	Colour	Lustre	Hardness	Specific gravity	System	Optical characters	n	N_g-N_p	Chief elements	Minor elements	Admixtures
Ampangabeite, villages of Novo-Yelisseyevka and Dolinskoye	Light-brown to brownish-yellow	Vitreous	4—4.5, brittle	3.92, upon ignition 4,0	Rhombic ? or tetragonal, metamikt	Transparent, isotropic, upon ignition anisotropic	1.89—2.00, upon ignition 2.06	About 0.01	(Nb, Ta), Fe, Y—Er, U, H_2O	Ti, Ca, Ce-Th, Mn, Pb	—
Ampangabeite, Madagascar	Variable black-fallow-reddish to brown-yellow	Strong, vitreous	4, brittle	Variable, 3.348—4.644	Rhombic, metamikt	Do	Variable, 1.89—2.13	Do	Nb, Ta, Fe, Y—Er, U, H_2O	Ti, Th, Ce, Mn	Ca, Sn W
Betafite, Madagascar	Greenish-brown to yellow	Do	Do	Variable, 3.75—5	Cubic, octahedral or rhombic-dodecahedral	Transparent, isotropic, upon ignition same	1.92	—	Nb, Ta, Ti, U, Ca, H_2O	Fe, Y, Ce, Th	Mg, Al, Sn
Blomstrandite, Madagascar	Do	Do	Do	Variable, 4.74	Cubic, octahedral	Transparent isotropic	High	—	Ta, Nb, Ti, U, Ca, H_2O	Fe, Y, Ce	Mg, Mn, Bi, Sn

nite without titanium. From the chemical standpoint a simplified formula is given as $RO \cdot Nb_2O_5 \cdot 3H_2O$, with a possible presence of TiO_2 replacing Nb_2O_5. The main components are Fe, Y—Er group, U, Nb, Ta, H_2O. Minor admixtures are (in varying amounts): TiO_2 (5.22—0.12 per cent), ThO_2 (2.50—1.30 p. c.), Ce_2O_3 (5.0—0.60 p. c.), MnO (1.53—0 p. c.). The UO_2 content is 18.31—11.98 per cent. The varieties are produced by a different degree of hydration. The specific gravity, optical properties, *etc.* vary accordingly (see table).

The ampangabeite from the pegmatites near the villages of Novo-Yelisseyevka and Dolinskoye was found to represent small grains and segregations up to 5—15 mm, highly varying in colour but chiefly light-brown or brownish-yellow, with a greenish shade.

Around the grains, cream-coloured, very brittle crusts of an alteration product are observed; in this case the mineral is considerably lighter (more yellow) towards the periphery of the grains. In the feldspars round the mineral grains a change of colour caused by the radioactivity was observed. No crystals were encountered, but some segregations have an elongated finger-like appearance, and in cross-section form as it were a rectangle with considerably rounded corners. In some (very rare) cases also sections of as it were platy rectangular crystals were encountered, which make think of a possible rhombic (or tetragonal) system of the mineral rather than of a cubic system characteristic of betafite-blomstrandite. At the edges of the grains the mineral is generally translucent. Fracture uneven to conchoidal. Colour of the streak light, brownish-grey. Lustre vitreous. Hardness 4—4.5. Brittle. Specific gravity, as determined by a simplified picnometric method in alcohol, is 3.92 ± 0.02 (of the brownish-chestnut variety). Upon ignition to 850—900°C the mineral becomes opaque, brown, cracked, the colour of the streak changing to a brownish-yellow. The specific gravity somewhat increases, closely approaching 4.0.

An optical examination of the mineral by the immersion method revealed the following properties: the mineral is transparent, reddish-brown in colour, in very thin splinters nearly colourless, fallowish-yellow. The mineral grains are stuffed with submicroscopic inclusions reddish-brown in colour and sometimes with grains of an opaque pigment (possibly these are inclusions of columbite). It is isotropic (metamikt). Refractive index is very high; for brownish-yellow grains $n = 1.89 \pm 0.04$; for dark reddish-brown grains $n = 2.00 \pm 0.03$. Upon ignition the mineral reveals a distinct pyromagnetic effect, and upon ignition to 850—900° C remains transparent, reddish-fallow or yellow. It becomes distinctly anisotropic, that is, resumes a crystalline structure. Small fragments of the mineral transform into aggregates of minute-polarizing grains, sometimes into lamellar (elongated) anisotropic areas. Interference colours are grey, of the first order ($N_g - N_p \simeq 0.01$). No cleavage is manifest. Refractive index becomes higher: $n = 2.06 \pm 0.01$.

The optical investigation of the ampangabeite from Madagascar (the brown variety) simultaneously carried out by the present author yielded a similar result.

A study of the chemical composition of the ampangabeite was carried out by the microchemical method. The determinations were made on the same sample, with equal volumes of the solution in each determination, owing to which some quantitative data can be obtained.

The mineral can easily be decomposed by melting with KOH, NaOH, borax and $KHSO_4$. Upon boiling with concentrated H_2SO_4 it is completely decomposed, a small white precipitate being formed. In concentrated HCl it is decomposed upon boiling, under the formation of a white precipitate and a yellow solution. The microchemical study yielded the following results: SiO_2, very little (possibly from a silicate inclusion); TiO_2, little (1—5 p. c.); $(Nb, Ta)_2O_5$, very much (over 20—30 p. c.); Al_2O_3, none; $Fe_2O_3 + FeO$, much (about 10 p. c.); CaO, little (1—5 p. c.); MgO, none; Y_2O_3 group, much (about 10 p. c.); Ce_2O_3—ThO_2 group, very little (less than 1 p. c.); UO_2, much (about 10 p. c.); PbO, little (1—5 p. c.); CuO, none; ZnO, none; H_2O, much (about 10 p. c.).

The data obtained by the author coincide to a considerable degree with those of an X-ray and chemical study carried out by I. B. Borovsky, and thus

leave no room for doubt as to the correctness of the determination of the chemical nature of the mineral. The main physical and chemical properties of the minerals betafite, blomstrandite, ampangabeite and the investigated mineral from Yelisseyevka, tabulated and compared, along with the data presented above, permit of the following conclusions:

1. Some segregations of the mineral have an elongated shape resembling the shape of rhombic or tetragonal crystals. Upon passing from a metamikt condition to a crystalline one (upon heating) they acquire optical properties similar to those of rhombic (samarskite, euxenite, ampangabeite) and tetragonal (fergusonite) minerals, as a result of which it cannot be referred to cubic niobotantalates.

2. The external characters (colour, hardness, lustre, specific gravity) resemble more closely rather those of ampangabeite than those of the cubic niobotantalates of the betafite group.

3. The chemical composition corresponds to a hydrous niobotantalate of uranium, iron and yttrium group, with a partial replacement in the anionic group of $(Nb, Ta)_2O_5$ by titanium, and in cations, by an admixture of Mn, Ca and Pb. Particularly interesting is the last-mentioned feature; however, there is nothing unusual in it, since the mineral is very rich in U. These data correspond fairly well to the composition of ampangabeite and show a considerable difference from the composition of the cubic niobotantalates of the betafite group, since the latter are niobotantalo-titanates of uranium and calcium, and contain the yttrium group and iron only as minor constituents.

The A. P. Karpinsky Geological Museum.
Academy of Sciences of the USSR.

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PLANT PHYSIOLOGY

A GRAVIMETRICAL METHOD FOR DETERMINING THE ACTIVITY OF GROWTH SUBSTANCES

By E. V. BOBKO and N. I. YAKUSHKINA

(Communicated by D. N. Prianishnikov, Member of the Academy, 1.XII.1944)

Following Went and Thimann ([5]) we understand by the activity of growth substances, either natural or synthetic ones, their ability to produce an irreversible increase in the volume of cells connected with the intake of water. After Sachs' well-known scheme, the phenomenon of growth can be subdivided into four phases, *viz.*: 1) organization, 2) differentiation, 3) elongation and 4) maturation. It is well known that any of these stages may be influenced by growth substances; the majority of studies, however, are dealing with the 3rd phase (elongation). This is but natural, for it is just at the elongation stage that the relation between the treatment and the reaction of the plant is especially manifest and can easily be recorded, and indeed a variety of methods have been suggested for doing so. An attempt to summarize the most important among them has been made in Table 1.

As may be seen from the table, only Cholodny's photometrical method permits of a direct determination of the quantity of water entering the plant, while all the other methods involve recalculation and can ensure no precise results. Unfortunately, Cholodhy's method is rather complicated and does not fit for mass determinations. Went's methods won the widest application, since they permit to evaluate the energy of growth from the angle of the bend of the coleoptiles of oats, or of the fragments of the stem of peas.

Despite their apparent simplicity, the two methods are very cumbersome and require a great skill in such procedures as the application of blocks or splitting of fragments, *etc.* Their principal disadvantage consists, however, in the fact that the measurements of the angle of bend cannot be done with a sufficient accuracy, while the computation of volume from the angles is a rather complicate matter.

It appeared desirable therefore to have resort to a new principle, which would free the method from the drawbacks inherent in Cholodny's method and in the two methods of Went, yielding at the same time sufficiently accurate results.

Principle of the Gravimetrical Method. Fragments of stems of peas are weighed in weighing glasses and placed into the solution of the substance to be tested. After a certain time interval the fragments are taken out, blotted with filtering paper and weighed again. The increment in weight against the control (tap water) expressed in per cent to the initial weight, serves as a measure of the activity of its growth in the substance tested.

Table 1

Methods for Determining the Activity of Growth Substances

Plant species and pre-treatment	Object of measurements and method	Author of the method
Avena coleoptile: decapitation, lateral contact of an agar block containing the substance to be tested	Angle of bend of coleoptiles (by means of a protractor)	Went, 1928[6]
Seedlings of peas: decapitation, sectioning of 3-cm long pieces, splitting to 2 cm, immersion into solution to be tested	Angle of bend of the two halves of the split stem (with the aid of a protractor)	Went, 1937[7]
Avena coleoptile: fragments of decapitated ones immersed with their ends into solution to be tested	Elongation of the coleoptiles (with the aid of a horizontal microscope)	Bonner, 1933[1]
Avena coleoptile or seedlings of sunflower: fragments of stems immersed with their lower ends into the solution of the substance to be tested	Volume of water taken in (with the aid of a microphotometer)	Cholodny, 1929[2]
Seedlings of the *Vicia Faba* decapitated epicotyles covered from above with lanoline containing substances to be tested	Increase in diameter of the upper part of the epicotyle (by means of a horizontal microscope)	Laibach, 1935[3]
Seedlings of kidney beans: covering of the first internodes with rings of lanoline paste mixed with the substance to be tested	Increase in length of the first internode (with the aid of a ruler)	Mitchell, 1941[4]

Technique of Determination. Carefully selected seeds of peas (with the aid of sieves, after weight and after external appearance), are soaked in tap water during 20 hours. The swollen seeds are planted to an equal depth into sand placed in appropriate containers and moistened to 20 per cent of the total moisture capacity. The containers are placed into a thermostat installed in a dark room and kept there for 7 days, at a temperature of 22° C (to $\pm$1 °C), at a relative humidity of about 85 per cent.

During this time the seedlings attain 10—12 cm in length, and develop 2 scales and an apical bud. The distance between the apical bud and the upper scale should be no less than 30 mm, and between the apical bud and the first leaf, no more than 5 mm.

With the aid of a special double knife made of two safety razor blades a section 30 mm long is excised at a distance of 5 mm from the top. Six sections are put into a previously weighed, dry weighing glass 30 mm wide and 45 mm high, closed with a well-ground stopper and weighed on an analytical balance to 0.2 mg. Then 20 ml of the solution to be tested is poured in, and the weighing glass is placed again into the thermostat. After 20 hours the solution is poured out through a cheese cloth put on a funnel, the sections are quickly blotted between two cotton cushions covered with filtering paper, transferred into another clean and previously weighed weighing glass and weighed again. All these operations are performed in red light.

The increment in weight recorded by the second weighing corresponds to the amount of water taken in by the sections. The arithmetical mean from parallel determinations is taken and expressed in per cent to the initial weighed portion. Prior to comparing individual lots, the increments in the control (tap water)

are subtracted from each of them. In our experiments the control was usually found to make up about 10 per cent to the initial weight.

Let us give here as an example the results of one of our experiments, where various concentrations of heteroauxine were tested (indol-3-acetic acid). These results are summarized in Table 2.

Table 2

Effect of Concentration of Heteroauxine Solution in Tap Water upon Water Intake by Sections of Peas

Concentration of heteroauxine, mg/l	Increase in weight of fragments of peas, in % to initial weight	Increment due to heteroauxine referred to control, in %
0	12.8 ± 1.1	—
0.01	16.2 ± 1.0	3.4
0.05	19.9 ± 0.9	7.1
0.10	22.4 ± 1.0	9.6
0.50	28.5 ± 0.2	15.7
1.0	38.6 ± 0.8	25.8
5.0	40.2 ± 0.4	27.4

As may be seen from Table 2, the amount of water taken up by the fragments of the stems of peas grows regularly with the increase in the concentration of heteroauxine.

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PLANT PHYSIOLOGY

TRANSPLANTATION AS APPLIED TO THE STUDY OF NUTRITION OF DIFFERENT PLANT SPECIES

By A. V. SOKOLOV

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If one plant species is grafted to another, the scion is supplied with mineral elements whose intake depends on the properties of the roots of the stock. Different plant species do not respond in the same way to the presence of a particular element. Calciophobe plants do not stand high concentrations of calcium. Some plants are injured by such concentrations of $H^{\cdot}$ or $Al^{\cdot\cdot\cdot}$ in soil solution as are easily endured by others. The sensitivity of plants to Cl, Mn, B, Fe also differs with the species. The reason, why different species give a different reaction to a given composition of the soil solution, is not known in most cases.

By grafting a plant of a definite type of mineral nutrition to a plant of another type it is possible to differentiate the effect produced by the element studied upon the root system from that produced upon the exchange in the leaves. By grafting a calciophobe plant to a non-calciophobe one, or a plant sensitive to high concentrations of $H^{\cdot}$, $Al^{\cdot\cdot\cdot}$ or Cl' to a resistant one, it must be possible to find out whether the reason for the difference in the reaction lies in the properties of the root system, or in the peculiar exchange taking place in the leaves.

The existence of a relation between the quantity of mineral substances in the scion and the kind of the stock has been demonstrated by more than one experimenter. Different species react differently to the soil conditions, according to whether they grow on their own roots, or are grafted to a stock (1).

For experiments involving grafts such pair of plants should be selected which would admit of mutual grafting and differ as to the type of their mineral nutrition. Common, readily practicable grafting of potato to tomato or of water melon or cucumber to pumpkin are of little interest in our case, as the plants do not differ sufficiently as to the type of their mineral nutrition. On the other hand, such plants as lupine and peas are of great interest to agrochemists and physiologists. The possibility of grafting these plants to each other was demonstrated by V. I. Sokolova. They are generally known to differ sharply in a number of agrochemical features. Lupine is a calciophobe plant, sensitive to an excess of chlorides, but easily resisting to acid soils and considerable concentrations of Al and B. The pea is no calciophobe plant, its reaction to calcification of the soil being a positive one. It survives well to considerable concentrations of chlorides, but is very sensitive to an excess of Al and B in the nutrient solution.

Our experiments involved grafts of the following two species of peas: blue lupine (*Lupinus angustifolius*) and yellow lupine (*Lupinus luteus*).

Although grafting is practicable in either direction, yet in our experiments the percentage of successful grafts was higher with peas as a stock. The tech-

nique of grafting was a relatively simple one. The stem of a young pea plant is cut across at the height of the 2nd or 3rd leaf. With a safety razor blade a split is made about 10 mm deep. The stem of lupine bearing one or two pairs of leaves is inserted into the split with the wedge-like end. The point of grafting is tightly wrapped with a ribbon of raphia 5 mm broad. Care should be taken in order to keep the place of grafting out of the liquid (in water cultures). In soil or sand cultures it must not be overmoistened while watering. The raphia should not be taken off until three or four weeks have passed. The grafts should not be exposed to intense sunlight during the first days after the operation; it is well to cover them with a glass bell bearing an opening for the circulation of air.

In water-cultures good results were obtained only in the case of lupine grafted to peas, whereas grafts of peas to blue or yellow lupine survived in a few cases only. To conduct these experiments a whole series of quite healthy grafts of exactly the same age is necessary. We give here a description of one of the experiments. Seeds of peas (variety Evergreen Folghiera) and of blue lupine (pure line bred at the Novozybkov station) were germinated between sheets of filtering paper and, after the roots had reached 2—3 cm in length, were placed on a paraffined net into containers filled with tap water, the latter being changed daily. After grafting was done, the plants were kept during two days in shade, covered with glass bells. After five days the glass bells were removed, and the necessary number of grafts suitable for experiments were selected; these were distinguished by having developed the 2nd pair of leaves.

All the experimental plants were grown during the first day of the experiment (14.IX) on Hellriegel'mixture, the degree of all the ingredients being reduced to 40 per cent of the original value. The following minor elements were added: B, 0.08 mg/l; Mn, 0.16 mg/l; Cu, 0.08 mg/l and 1 mgl of the 1 per cent solution of iron citrate. Three plants were left for each pot of 1.2 l capacity. On the second day, half of the plants were transferred to a nutrient solution without P_2O_5, and another, to a nutrient solution without P_2O_5 but containing 6 mg/l of Al in the form of $Al_2(SO_4)_3$. The solutions containing no Al were acidified with H_2SO_4, to make the pH equal in all the pots. Aside from grafts there were also experimental plants of pure blue lupine. Each set was run in quadriple replication. On the 16th of September all the plants were placed again on full nutrient solution. When the plants were transferred from one solution to another, their roots were washed with water. The alternation of the solutions was continued till the 10th of October, when the plants were harvested. At this moment the plants had 6—7 pairs of leaves.

The results of the experiment are presented in the table.

Weight of Plants on the 25th Day of Experiment

Pot No.		Experimental scheme	Average number of leaves per plant	Dry weight of a single plant	
				stems and leaves	roots
1 — 4	Blue lupine grafted to pea . . .	without Al	13	0.44 ± 0.04	0.16 ± 0.01
5 — 6	Same	Al 6 mg	13	0.34 ± 0.01	0.14 ± 00.1
9 — 10	Blue lupine . . .	without Al	10	0.32 ± 0.02	0.11 ± 0.01

In spite of the short period of the experiment, the effect of Al was quite noticeable. In the presence of Al in the nutrient solution the blue lupine developed somewhat better than without it. On the other hand, when grafted on pea roots, lupine developed better without Al. The adverse effect of Al is thus due to its

action upon the root system. In contrast to the observation by Meshcheriakov[2], there could be noticed no morphological modifications of Al, but the ill effect of Al was nevertheless connected with its action upon the roots.

Another experiment was carried out with soil cultures. On the thick chernozem of the Grakov experiment plot, when 2 per cent of lime was added to the soil, the yellow lupine showed a strong leaf chlorosis which ultimately led to a complete withering of the plants, in spite of the microelements introduced. When peas were grafted to a lupine plant which was already suffering from chlorosis, the former continued developing and attained the state of blooming. Peas grown on their own roots on chernozem with the addition of lime developed normally and did not suffer from chlorosis. By grafting lupine to peas under similar conditions plants were obtained which did not suffer from chlorosis. Yellow lupine developed on the roots of peas under such conditions which would not allow it to grow if grown on roots of its own. The phenomena of calciophobia of lupine are, consequently, also connected with the activity of the root system. The roots of peas had taken from the soil such mineral elements as did not cause chlorosis of the leaves; conversely, the roots of lupine under similar conditions also supplied the pea-plant with such a set of elements as caused no chlorosis. The phenomenon of calciophobia is, consequently, due not only to some peculiar exchange in the leaves of lupine, but also to a certain specific activity of its roots; lupine is known to absorb extremely large quantities of calcium[3].

Dolgoprud Agrochemical Experiment Station.
Institute of Fertilizers and Insectofungicides.

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PLANT PHYSIOLOGY

EFFECT OF SOLUBLE NITROGENOUS COMPOUNDS UPON FORMATION OF NODULES ON ROOTS OF LEGUMINOUS PLANTS

By M. CH. ČAJLACHJAN and A. A. MEGRABJAN

(Communicated by A. A. Richter, Member of the Academy, 3.XII.1944)

The nitrogen nutrition of leguminous plants involves both the absorption of the nitrogenous soil solutes by the roots and the activity of the root-nodule bacteria which penetrate into the root tissues, propagate there and fix the free nitrogen of the atmosphere. In their studies on the effect of soluble nitrogenous compounds upon the activity of the bacteria and the formation of root nodules Hiltner (7), Laurent (8) and other early writers had pointed out the harmful effect of the nitrogenous compounds upon the development of the bacteria and the formation of root nodules. Subsequent, more detailed studies by Fred and Graul(6) and by many others (1) led to the conclusion that the increase in the mineral nitrogen content of the soil produced a negative effect upon the formation of root nodules. There still exists, however, an opposite view advocated among others by Albrecht (5); there are also observations showing that by introducing nitrogenous fertilizers no reduction in the formation of root nodule is caused.

In connexion with our more general studies on the effect of nitrogenous nutrition upon the rate of the development of the plants, *Leguminosae* included, we have subjected this problem to an experimental trial. The work was carried out in 1942—44, in a greenhouse and in the laboratories of the Armenian Agricultural Institute, Division of plant physiology and microbiology.These studies led us to a conclusion that the formation of nodules on the roots of leguminous plants proceeds more intensely in the case of a low content of soluble nitrogenous compounds (3).

Similar results were obtained in subsequent experiments on lupine, *Ervum vicia* beans, Turkish pea, clover and alphalpha carried out by the method of sand and soil cultures, the dosage of nitrogenous compounds being regulated by periodical addition of ammonium nitrate.

The question arises as to the initial causes of the checked development of the root nodules, *i. e.* whether it is due to the presence of large quantities of mineral nitrogen in the substratum, which checks the development of the root nodule bacteria in the soil (sand) and their penetration into the roots, or whether the reason lies in the presence of a large quantity of nitrogen in the plant itself, which prevents the inoculation by the root-nodule bacteria and their development within the root cells. This problem was usually studied by comparing the effect of definite concentrations of nitrates upon the development of root nodules and the vitality of the root-nodule bacteria in the soil (8,9). Korsakova and Konokotina alone made an experiment with lupine in which the number of root nodules formed

was recorded; this study led the authors to a conclusion that the salts of ammonia act upon the bacteria after the latter had penetrated into the root system of the leguminous plant.

Seeking for a solution of this problem, experiments on a group of species were arranged, based upon the administration of high doses of nitrogen and on a careful weighing and counting of the root nodules formed. The technique was as follows. The seeds of the leguminous plants were germinated in washed saw dust in wooden boxes until the roots attained a length of 10—12 cm, after which the seedlings were transferred to shallow 13-cm clay pots filled with moist sand containing a nutritive mixture of the mineral substances. The aperture in the bottom of the pot was covered with two layers of cheese-cloth, and the root tip was pushed through it into the nutritive solution contained in a glass jar placed with its perforated cover under the pot. The apex of the root grows very rapidly, so that a kind of a two-storey root system was formed, the upper part of which being in the pot filled with sand and the lower one composed of younger apical parts of the root, contained in the aqueous solution filling tha glass jar. By varying the composition of the nutrient mixtures in the sand and in the solution it was possible to change independently from each other the inorganic and organic compounds surrounding the upper and lower zones of the root system. This method was termed by us the two-storey root culture.

Two-storey culture of *Ervum vicia* roots in a mounted aspect. The upper storey of roots, in a sand vessel; the lower storey, in an aqueous solution in a glass jar

In our case the variation was limited to the nitrate of ammonia, which was either added or not added to the sand or aqueous solution.

Fig. 1 represents a plant of *Ervum vicia* grown by the method of two-storey root culture; the roots are well developed both in sand and in solution.

The experiments with soy-bean *(Soja hyspida)* and French lentil *(Ervum vicia)* were conducted in the autumn of 1943 in front of large windows of the laboratory, after the following scheme: 1) no nitrogen was introduced into the sand or the aqueous solution $\left(\frac{-N}{-N}\right)$; 2) no nitrogen was introduced into the sand, while two dosages of N were added to the aqueous solution $\left(\frac{-N}{+N}\right)$. Inoculation with the strains of the corresponding bacteria was done in the sand (upper root storey). Each experiment was repeated five times. The record of the development of the root nodules upon the roots within the sand were taken in December; data on the development of root nodules are contained in Table 1.

Table 1

Effect of Ammonium Nitrate Entering through the Lower Root Storey upon the Formation of Root Nodules on the Roots of the Upper Storey

Plant	Experimental scheme		Root nodules in sand per one plant	
	upper storey	lower storey	number	weight, g
Soy-bean	—N	—N	4	0.009
	—N	+N	none	none
French lentil	—N	—N	4	0.012
	—N	+N	none	none

This experiment shows clearly that no soluble nitrates are present in the sand, the formation of root nodules does not take place unless mineral nitrogen passes into the root cells from the lower root storey. In case the root cells are enriched with soluble nitrogen, the development of the root nodules is detained, in spite of the absence of nitrogen in the sand surrounding the roots.

During the summer of 1944 experiments after the same method were conducted with soy-bean, *Ervum vicia*, peas (*Pisum sativum*) and beans (*Phaseolus vulgaris*). The upper storey of the roots of these plants was kept in sand containing the Prianishnikov nutrient mixture, nitrogen being completely excluded from it; the lower storey was grown in an aqueous solution of the same nutrient mixture, with 3 dosages of different forms of nitrogen compounds, *viz.* sodium nitrate $NaNO_3$, potassium nitrate KNO_3, ammonium nitrate NH_4NO_3, ammonium sulphate $(NH_4)_2SO_4$, asparagin, control (no N). Two experiments were arranged with *Ervum vicia*, the one after the general scheme described above (22.VI—22.VIII) and an other with 2 dosages of nitrogenous compound introduced into the aqueous solution (22.V—22.VI). The solutions contained in the jars were changed every week, air being supplied daily. Inoculation with the strains of the corresponding bacteria was done in sand at the start of the experiment. The experiment was carried on in three-fold replication.

The young plants were kept under these conditions during a month; after this period the length of the stem and roots (in sand and aqueous solution) was measured, the number and weight of the root nodules on the upper root storey were recorded and the dried upper parts and the roots of the plants were weighed. At an early period of the experiment the control plant showed a lighter green colour as compared with the experimental ones which had received nitrogenous compounds *via* lower root storey; but toward the close of the experiment this difference was levelled out. The roots of the upper storey in sand were less developed in the control plants than in the experimental ones: a pronounced inhibition of the root growth of the lower storey was observed in the aqueous solution when asparagin and ammonium sulphate were introduced.

The data on the number and weight of the root nodules are presented in Table 2.

Table 2

Effect of Different Forms of Soluble Nitrogenous Compounds Supplied to the Plant *via* Lower Root Storey upon Formation of Root Nodules on the Upper Root Storey

Plant	Form of nitrogenous compound supplied to lower storey												Duration of experiment
	control (no nitrogen)		$NaNo_3$		KNO_3		NH_4NO_3		$(NH_4)_2SO_4$		asparagin		
	Development of root nodules on upper root storey per 1 plant												
	number	weight, g	number	weight, g	number	weight, g	number	weight, g	number	weight, g	number	weight, g	
Frenchlentil	4	0.008	1	0.003	none		2	0.005	none		none		22.V—22.VI
» »	2	0.008	none		»		1	0.003	»*		»		22.VI—22.VII
Soy-bean .	1	0.02	»		»		none		»		»		6.VII—6.VIII
Beans . .	24	0.02	»		»		»		»		»		20.VII—20.VIII
Peas . . .	4	0.006	»		»		»		»		»		10.VI—10.VII

* One plant developed two nodules weighing 0.004 g.

Table 2 shows that when the plant tissues are supplied with soluble nitrogenous compounds *via* lower root storey, the development of the root nodules on the upper root storey is inhibited, although no soluble nitrogen is present in the surrounding sand.

The experiments here described give thus the following answer to the question raised: the suppression of the formation of the root nodules and consequently the prevention of the penetration and development of the root-nodule bacteria in the roots of leguminous plants is not controlled by the amount of the soluble nitrogen contained in the substratum, but by the nitrogen which had already penetrated into the tissues of the plant. Like in the case of the effect of the day-length studied by us earlier ([4]), the agents of the surrounding medium modify the physiological condition of the plant, and this latter in its turn controls the susceptibility of the plant to inoculation with root-nodule bacteria. If the internal conditions favouring the formation of root nodules are the rich content of carbohydrates and growth substances ([4]), the presence in the tissues of a large quantity of soluble nitrates is, on the contrary, an agent acting adversely upon the penetration of the bacteria into the root cells and upon the formation of root nodules.

In order to obtain nitrogen the leguminous plants developed in the course of evolution an adapting ability to a symbiosis with the nitrogen fitting bacteria; but this very nitrogen plays an outstanding rôle in the mechanism regulating in the ontogenesis the relations between the leguminous plant and the root-nodule bacteria.

Department of Plant Physiology and Microbiology.
The Armenian Agricultural Institute.
Erevan.

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ZOOLOGY

CHALCALBURNUS CHALCOIDES IRANICUS SUBSP. NOVA FROM THE CASPIAN COAST OF IRAN, AND SOME ZOOGEOGRAPHICAL PROBLEMS OF THE SOUTHERN PART OF THIS SEA

By A. N. SVETOVIDOV

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The fish fauna of the southern part of the Caspian Sea is of great interest because of its outspoken endemic nature. Among the fresh-water fishes which are of little interest to us, there are up to 10 species and 5 subspecies encountered exclusively in rivers running into the southern part of the Caspian Sea: these fishes will not be considered here. We shall dwell in this note solely upon marine (more exactly speaking, brack-water), anadromous and semi-anadromous fishes. Among the marine, anadromous and semi-anadromous fishes peculiar to the southern and partly to the middle region of the Caspian Sea, should be classed: *Acipenser güldenstädti persicus* (Borodin), *A. stellatus stellatus* n. *cyrensis* Berg, *Caspialosa caspia knipowitschi* Iljin, *C. caspia persica* Iljin, *C. brashnikovi sarensis* Mikhaylovsky, *C. brashnikovi orientalis* Mikhaylovsky, *C. brashnikovi autumnalis* Berg, *C. brashnikovi kisselevitshi* Bulgakov, *C. brashnikovi nireli* Morosow, *C. brashnikovi grimmi* (Borodin), *C. curensis* (Suworow), *Rutilus rutilus caspicus* n. *kurensis* Berg, *R. rutilus caspicus* n. *knipowitschi* Pravdin, *Aspius aspius taeniatus* (Eichwald), *Barbus capito capito* (Güldenstädt), *Abramis sapa bergi* Belyaeff.

Many of these fishes (for example, *A. güldenstädti persicus*, *A. aspius taeniatus*) enter also the middle and even the northern part of the Caspian Sea, while others (for example, *Barbus capito capito*, *Abramis sapa bergi*) are peculiar to rivers of the western coast of the middle part of the sea. As may be seen from the above list, the endemic nature of the fish fauna of the southern part of the Caspian Sea is evidenced by the presence of low taxonomic units (subspecies and nationes). We encounter here a single endemic species, *viz. Caspialosa curensis*, whose specific differentiation seems rather doubtful*.

From among the fishes listed above, special interest should be attached to *A. sapa bergi*. By number of its characters this fish closely approaches the subspecies *A. sapa aralensis* (Aral Sea) rather than the subspecies distributed in the remaining part of the Caspian (*A. sapa sapa*). A similar affinity is revealed in *A. aspius taeniatus* with respect to which the form from the Aral Sea is considered as a natio only (*A. aspius taeniatus* n. *iblicides*), whereas the form encountered in the middle and northern part of the Caspian Sea is raised to the rank of a subspecies (*Aspius aspius aspius*). A similar taxonomic position is occupied by *Ch. chalcoides* from the Caspian coast of Iran, as may be seen

* When examined more closely, this species may prove to be but a subspecies of *C. brashnikovi*.

from the data given below. These data are based upon the examination of 10 specimens collected by E. N. Pavlovsky, Member of the Academy, in a small river in the vicinity of town Shakhi (basin of the river Talar, running into the Caspian Sea west of the Gorgan Bay), and 6 specimens from the Gorgan Bay, collected by Derzhavin (4).

	The Caspian Sea				
	Western coast of middle part of the Caspian Sea*	The Kura River**	Basin of Talar River	Gorgan Bay***	Aral Sea (Muynak)**
Number of scales in l.l.	—	72 — 70	54 — 64	(57)60 — 68)	56 — 72
	(63.6)	(—)	(59.5)	(63.8)	(63.1)
In % of body length					
Head length	19.5 — 22.5	—	20.1 — 21.8	19.4 — 20.7	—
Length of caudal peduncle	(21.0)	(19.3)	(20.8)	(19.9)	(21.6)
	—	19.0 — 26.0	20.7 — 23.3	19.0 — 22.6	18.0 — 26.0
		(22.4)	(21.8)	(20.6)	(21.4)
Depth of body	—	21.0 — 28.0	15,3 — 16,8	21.1 — 23.3	18,0 — 25.0
		(23.7)	(16.1)	(21.8)	(21.0)
Depth of caudal peduncle	—	7.0 — 10.0	6.7 — 7.9	8.0 — 8.8	7.0 — 11,0
	(7.9)	(8.4)	(7.3)	(8.2)	(8.4)
Depth of dorsal fin . .	—	11.0 — 15.0	13.1 — 15.8	13.2 — 15.2	13.0 — 19.0
	(16.1)	(13.1)	(14.1)	(13.9)	(16.1)
Height in anal fin . .	—	7.0 — 11.0	9.3 — 11.1	8.1 — 10.6	8.0 — 14.0
	(12.6)	(8.6)	(9.9)	(9,4)	(10.6)
In % to head length:					
Diameter of eye	—	17.0 — 28.0	21.8 — 26.7	25.3 — 30.4	19.0 — 29·0
	(25.1)	(21.6)	(24.0)	(27.7)	(24.4)
Depth of head	—	65.0 — 81.0	61.7 — 70,4	66.4 — 74.4	59.0 — 81.0
	(64.8)	(71.7)	(65.6)	(69.8)	(70.0)

* According to data by Makhmudbekov (6), from 290 specimens.
** According to data by Markun (5), from 74 specimens.
*** According to data by Derzhavin (4), from 6 specimens. This writer has committed an error in his calculation of the mean for head length (19.3).

According to the number of scales along the lateral line, head length, length of caudal peduncle, depth of body and eye diameter, as well as to many other characters serving to distinguish the subspecies of *Ch. chalcoides* from one another, the species here considered, *Ch. chalcoides* from the Caspian coast of Iran, is found to be more closely related to the *Ch. chalcoides aralensis* than to the *Ch. chalcoides chalcoides* from the Kura River, type locality of *Ch. chalcoides chalcoides*; this it true both of the specimens collected by the present author, and of those examined by Derzhavin. *Ch. chalcoides* from the Caspian coast of Iran is more closely related to *Ch. chalcoides chalcoides* from the Kura River than to *Ch. chalcoides aralensis* by the depth of dorsal fin only, occupying an intermediate position as to the depth of its anal fin. The specimens from the Tala-River differ essentially from those collected at the Gorgan Bay and from *Ch. chalcoides aralensis* by their considerably deeper body, head and caudal peduncle. This is undoubtedly due to the fact that the specimens were collected at the end of the spawning period (ovaries and testes have been found nearly or althogether void), whereas the specimens collected at the Gorgan Bay were in the last stage of ripeness.

As has been shown by investigations carried out by A. Makhmudbekov (6), specimens of *Ch. chalcoides* from the coast of the middle part of the Caspian Sea differ materially from those from the Kura River. Makhmudbekov, however, refrained from separating it as an independent form on account of the possible occurrence in those rivers of several forms, while the specimens described by him had been caught in the sea and might therefore prove heterogeneous. According to various characters, such as the number of scales in the lateral line, head length,

depth of dorsal fin, eye diameter, the *Ch. chalcoides* from the rivers of the western coast of the middle part of the Caspian Sea approaches, like *Ch. chalcoides*, from the coasts of Iran, the Aral form, from which it is distinguished in the depth of the anal fin, while from the Iranian it is distinguished also by the depth of the dorsal fin.

We thus see that *Ch. chalcoides* from the Caspian coast of Iran differs from *Ch. chalcoides chalcoides* from the Kura to the same extent as *Ch. chalcoides aralensis*; at the same time it differs essentially from the latter by the depth of its dorsal and anal fins. Accordingly, it should be classed, like *A. aspius taeniatus* n. *iblioides* and *A. sapa bergi* as an independent form, a subspecies whose description is given below.

Chalcalburnus chalcoides iranicus, sbsp. nova.

D III 8, A III 14—15, sp. br. 18—22, d. phar. 2.5—5.2, 1.1. 54—64. For the rest of characters cf. table.

Type ♀, body length 226 mm (without caudal fin, total length 263.5 mm), 1.VII.1942.

The specimens from the basin of the Talar River have a strongly prominent jaw with a soft process at the top. A similar soft process at the top of the lower jaw is observed also in *Ch. chalcoides aralensis* ([1], Fig. 418) and in *Ch. chalcoides derjugini* ([1], Fig. 417).

Whether *Ch. chalcoides iranicus* is or is not distributed throughout the Iranian coast of the Caspian Sea, is not known at the present time. Derzhavin ([4]) had at his disposal specimens from the western part of the Caspian coast of Iran (Khalikey and Siazan Rivers, running into the Enzely Bay, Shalman River); as a matter for regret, however, he gives no corresponding taxonomic data.

A biological feature characteristic of *Ch. chalcoides iranicus* is that its spawning is extended to a rather considerable period of time, its time and conditions varying greatly, besides. The fact that young in the earliest stages are encountered along the coast of Iran throughout the year, made Ginzburg ([3]) assume that the spawning proceeds there nearly throughout the year.

This assumption finds support in the fact that adult *Ch. chalcoides iranicus* with almost ripe sex products were encountered there ([3]) both in summer (July) and in winter (February). Derzhavin ([4]) happened to observe spawning specimens of *Ch. chalcoides iranicus* in the Gorgan Bay at the beginning of June, which made him believe that the season of spawning of this fish is by some 1—2 months more advanced there than it is in the Shalman River and in the rivulets of the Enzely Bay. A protracted spawning period is typical of *Ch. chalcoides aralensis*, as well([2]). Let us remind in this place that in the Terek River *Ch. chalcoides chalcoides* is spawning in May; *Ch. chalcoides danubicus* in the Kuban River, in the middle of May ([2]). Both subspecies enter the rivers high upstream (the Kura River as high as the Khram River and the Aragua River, the Terek higher than the mouth of the Sunja, and the Kuban as high as the mouth of the Laba River). According to data by Derzhavin ([4]), *Ch. chalcoides* does not penetrate high upstream the rivers of the Iranian coast. From his personal observations, as well as from information collected among local population, this writer is brought to suppose that in the Gorgan Bay *Ch. chalcoides* is spawning in the open bay, similar to what has been reported for the Aral Sea. According to our data, however, *Ch. chalcoides* spawns also in rivers, entering as high as 40 m upstream the River Talar. Thus, according to its biological features, *Ch. chalcoides* of the Iranian coast of the Caspian Sea is more closely related to the Aral species than to the species inhabiting the other parts of the Caspian Sea.

The Zoological Institute.
Academy of Sciences of the USSR.

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EXPERIMENTAL MORPHOLOGY

EXPLANTATION OF THE RUDIMENTS OF SKIN EPIDERMIS AND NEURAL PLATE

By J. A. VINNIKOV

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The rudiments of the neural plate and of the skin epidermis of *Amphibia* (axolotl and *Rana temporaria*) were studied by the tissue culture method in the hanging drop at the stages of gastrula, neurula, and caudal bud. In one set of experiments the explants were embedded into liquid medium, a drop of Holtfreter's solution. In another series the explants were cultivated in a solid medium consisting of a mixture of rabbit blood plasma and chick embryo or marrow extract hypotonized to an appropriate degree. Living as well as fixed material was studied, treated with the usual histological method. A total of about 20 experiments were carried out. The total number of the explants studied was over 120.

The ectoderm of axolotl is more or less uniform at the gastrula stage. The subsequent neurulation leads to a clearly marked differentiation of the neural plate consisting of stratified sheets of tall, prism-like, pigmented cells and cells filled with yolk, showing a very large number of mitosis. At a corresponding stage of development the material of the epidermal rudiment changes to an insignificant degree and is still composed of comparatively thin disproportional, two-layered sheet of embryonic ectodermal cells, flat or cubic in form.

The isolated pieces of the presumptive epidermis when explanted in the solid medium, showed an extensive growth on the 2—4 day of cultivation. Extensive epithelial membranes, layers, or strands made their appearance. Closely adjoining or overlapping polygonal elements in layers and strands were flattened out, or connected by means of intercellular bridges in thin membranes; at the same time they were isolated from one another by regular intercellular boundaries.

Owing to the development of the ciliar apparatus, the cells of the growing zone were intensely ciliating. Among them the rounded Leidig cells, filled with droplets of secretum and devoid of cilia and pigment, were clearly distinguishable. By the 20—25 day of cultivation, a cuticular border developed instead of the cilia which disappeared by that time. The amount of yolk and pigment granules in the cell protoplasm decreased. No other non-epithelial or complex structures could be observed in the growing zone. By the end of the second month such cultures, characterized by a constant epidermal histiotype of the growing zone (1), were usually fixed for histological investigation.

In the liquid explantation medium the transformation of the presumptive rudiment into epidermal epithelium was observed only in the case, where mate-

rial of some other rudiment, *e. g.* eye, pronephros, heart, *etc.*, was added. Within several hours the tissue introduced was found to be covered from all the sides by non-differentiated epidermis. This process of «epithelization» ([1, 2]) showed that the organotypic function of epidermis was manifest in the embryonic material before the beginning of cell differentiation. The interaction between the epidermis and the elements of the underlying rudiments, *i. e.* «epithelization», led to the development of a definite morphologically determined organ, corresponding to the determination of the rudiment within the heterogeneous explant, which was represented by a vesicle with epithelial wall and introduced tissue.

The organotypic coating function of the epidermis leads to the restoration and formation of an isolated inner milieu ([3]) in the explant, in which the morphogenetic processes go on under conditions of explantation. On the other hand, the epidermis itself was arranged on an appropriate mesenchyme substratum, which developed from elements of the rudiment introduced. Accordingly, its cytological and histologicad differentiation proceeded quite normally, leading eventually to the development of the epidermal coat, which was much similar to the epithelial layer of amphibian skin at corresponding stages of *in vivo* development.

It was a typical stratified epidermis with strongly expressed vertical anisomorphy ([1]) and large granular Leidig's elements. It also had a cuticular border, and was separated from the underlying connective tissue by a basal membrane.

It is interesting to compare the experimental results of *in vitro* explantation of a definitive epidermis of Garder's gland ([1]) with those of Lasarenko's investigation ([4]) on *in vivo* differentiation of the epithelium of salivary glands immersed into the inner milieu. In the first series of experiments under comparison the epithelium, in addition to extensive growth, showed a capacity of epithelization of the explant giving rise to multi-layered sheets. In the second case the epithelizing layers, formed anew from different parts of the salivary gland, nevertheless were ultimately found capable to produce outgrowths looking like excretory ducts which were completed by distal glandular parts, penetrating deep into the connective tissue. Thus, in Lasarenko's experiments the formative and cytological peculiarities of the epithelium were observed in the inner milieu of an organism.

The transformations in the tissue cultures of the neural rudiment extracted at the late gastrula and neurula stages were, in principle, quite different from those observed in the cultivation of the epidermal rudiment. In the solid medium the neural explants showed an extensive growth. In the growing zone there appeared numerous growing and differentiating pigment elements: melanophores, guanophores, and lipophores. There were also observed membranes composed of polygonal, bright and poorly pigmented elements possessing characteristic longitudinal «neural» nuclei. The membrane elements in the preparations fixed and treated in an appropriate way displayed a fine fibrilar structure. Thin neural fibres, sometimes branching and strongly refracting, developed from the central piece of the explant on the 4th—7th day of cultivation ([5]).

One succeeds to trace neurofibrils in the neural fibres on living material. The distal ends of the neurofibrils had terminal thickening («growing core»).

Their growth in the longitudinal direction is also sometimes accompanied by the splitting of the fibre in some place into 3—4 still thinner fibrils. In the small hollows of liquefaction of the growing zone there were occasionally observed characteristic cells similar to neuroblasts and attached by their long and branched processes to other elements of growing zone. However, both the neural fibres and the cells, similar to the neuroblasts, sooner or later disappeared, while the proliferating and mobile elements of the growing zone gave rise to a variety of structures of the glial type, described by Chlopin and others ([6, 7]). Thus, the histiotype of the neural rudiment was also observed in the embryonic material. It is fixed at a relatively early stage and simultaneously with the epidermal one.

In the liquid explantation medium the isolated parts of the neural rudiment became round, and transformed into transparent vesicles, inside of which there

were present spherical complexes of the cell arranged in disorder and showing for the most part the characteristic neural structure. The superficial elements of the vesicle were usually arranged in the substratum consisting of star-like cells of the mesenchyme. Unlike the epidermis, the covering layer of the explant consisted of a single layer of cells containing no Leidig's cells. The histological singularity of this covering layer gives some ground to speak of its ependimal origin. The development of the true ependimal covering was observed very rarely.

On the other hand, the explant was supplied with a covering only in part, or was lacking it at all. In this case the neural structures were directed into the explantation milieu ([8]). The neural structures inside the explant varied greatly.

They represented small complexes supplied with lumens. The cell elements, of which they were composed, were arranged in several layers, whose regular polar orientation was similar to that of the neural tube. The nucleus-containing protoplasmic regions bordered the lumen, while the fibrous process-bearing parts of protoplasm were directed to the opposite side, forming a kind of border veil ([9]). In some cases the neural complexes were represented by vesicles made from the flattened cells, very similar to the ear vesicles. The orientation of the neural cells was opposite in those parts of the explants which were naked and destitute of covering. In the latter case the nucleo-protoplasmic parts of the neural elements were directed into the outer explantation milieu. In accordance with Holtfreter's opinion ([8]), we are inclined to assume the possibility of a polarizing influence of the environment upon the structural arrangement of the elements of the neural tube. It is necessary to take into account, however, the polarizing influence of the inner milieu of the explant, which was not pointed out by this author. For the *in vitro* morphogenesis of the neural plate is important the position of its elements on the boundary of two phases, *i. e.* the explantation milieu or the milieu of the neural tube cavity itself, that immersed together with the neural plate, and the inner milieu of the explant formed by the tissues of the inner milieu.

At the gastrula and early neurula stages the neural material showed a similar behaviour *in vitro*, which is in agreement with the recent data of a number of authors ([10]).

As has already been shown, similar regularities of the spatial relation of the cell substratum also determine the organotypic differentiation of the epidermis which manifests itself in the strict polar relations of the cells that epithelize the explant and are arranged at the boundary between the external and internal milieu of the explant.

The factual data described above give reason to conclude that epidermal and neural material of the ectoderm is determined at an early stage of development. The differences between the material under consideration are observed as early as at the gastrula and neurula stages. The histological and cytological characteristics of these elements show a divergent development. The epidermal ectoderm is polarized from the underlying mesenchyme towards the external milieu (vertical anisomorphy). The cells of the neural tube are polarized in the direction from its lumen, *i. e.* from its own milieu, towards the surrounding mesoderm. Thus, the position of the cambial elements in both rudiments is an opposite one. The cytological peculiarities of the latters can also be observed when, under the explantation conditions, the morphogenesis of the whole rudiment is disturbed or absent, because of the experimental changes in the density of the explantation medium.

The divergence in the final cytological differentiation of the rudiments in question coincides, however, to some extent with the morphogenetic processes that take place in their development. The presence of the restricting covering tendency and polarity is also peculiar, to some degree and in a characteristic way, to the neural rudiment. This coincidence must be interpreted in terms of the common origin of the epidermis and neural plate from the ectoderm. The common origin of the rudiments under consideration affects not only the ontogenesis of

the skin epidermis and neural plate, but also the phylogenetic development.

It is necessary to point out, however, that the presumptive epidermis does still maintain its indifferent structure when the neural plate has already developed in medullary tube (early caudal bud). This peculiarity is to be kept in mind when analysing the various extraneural structures (placodes) arising in the subsequent from the presumptive epidermis.

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EXPERIMENTAL MORPHOLOGY

INFLUENCE OF LITHIUM CHLORIDE UPON HISTOGENETIC PROCESSES IN *ANURA*

By Z. S. KATZNELSON

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Modern developmental mechanics has at its disposal a very large number of facts concerning the early stages of development (the development of germinal layers, and the initiation of larval organs) and also concerning post-embryonic development. But there are scarcely any experimental data on the later stages of embryonic development, during which histogenesis and tissue differentiation take place.

It is now high time to supplement the data already accumulated in modern experimental morphology, which is, essentially, the developmental mechanics of organs, with new data on the developmental mechanics of tissues.

There are various correlations manifested in histogenesis which have not yet been studied. In order to undertake studying them it is necessary, first, to alter the usual correlation system observed during normal development. We are trying to do this by making use of various factors whose morphogenetic influence has either been established already, or can be suspected. By varying the environment and comparing the various types of correlational disturbance induced thereby in the tissues, we hope to be able to throw some light upon the general correlation mechanism of histogenetic development. Seeing that this subject is an entirely new one, general statements can hardly be made as yet, and we confine ourselves for the time being to the accumulation of experimental material.

The morphogenetic influence of lithium was established quite long ago by a number of authors, the first of whom was Herbst. Recently the morphogenetic influence of lithium upon amphibians has been studied by Lehmann (1) and Hall (2).

In previous works (3—4) the author of the present paper studied the action of lithium in the histrogenetic processes in amphibians. The present paper gives a short account of an analogous study made upon *Anura*.

Frogs' eggs at the late gastrula or early neurula stage were divided into two portions, each of which was placed in a dish containing 2 l of tap water. One of these portions served as a control; to the other 0.5 or 0.25 g of lithium chloride were added (making a LiCl concentration of 0.025—0.0125 per cent). Observations were recorded daily, and every day embryos were fixed with Fol's chromium-osmium solution, or with a chromium-acetate solution (5). As soon as well-defined changes appeared, some of the experimental embryos were transferred to pure water for a study of the regulative processes which set in under such conditions.

The material was then embedded in paraffin through clove oil, and sections 6 μ thick (frontal, sagittal and transverse) were stained into various tints with haematoxylin after M. Heidenhain's method.

The embryos treated with lithium chloride showed retarded development from the third and sometimes even from the second day on; the development of the caudal bud and the branchial tubercle is retarded, but the sucker develops normally.

On the 6th or 7th day of development the experimental larvae have pronouncedly underdeveloped tails and branchiae. A swelling appears on the ventral side of the body (a «ventral bladder»), and the body itself becomes more or less bent. Most of the surviving larvae (by this time many of them have died) have an underdeveloped mouth bay and olfactory pit. After this and up to the 9th or 10th day these larvae show no further change, but spontaneous bending can be observed in many of them between the 3rd and 8th days; this bending is somewhat less pronounced than in the control, and it disappears a day or two before the larva dies.

A microscopic study of the embryos with these «lithium morphoses» showed the following results:

1. In the nuclei of the embryos treated with lithium the number of chromatin granules decreased, and in the later stages (on the 5th day) the volume of the nucleus increased somewhat. But neither of these changes were as strongly expressed in frog embryos, as they were in those of the axolotl ([4]). On the other hand, the gradient of these changes can be observed quite clearly in frog embryos: they are best seen in the cell nuclei of the anterior part of the body, and gradually become unnoticeable toward the posterior part.

2. Lithium influences karyokinesis in different tissues differently. The mitoses in the epidermis cells disappear quickly, but in the cells of the mesenchyme, brain vesicles, eye cup and auricular vesicle they may still be present on the 5th or 6th day of the experiment. An analogous phenomenon was observed for the axolotl.

3. Differentiation in the epidermis tissue was pronouncedly inhibited. It remained in the two-layer stage, showing no signs of layer differentiation, which is typical for amphibians ([6, 7]). The only difference between the layers was a pronounced vacuolization in the cells of the surface layer. Since this results in an increase in the volume of the cells, some of the cells in the surface layer occur to be pushed out of the epidermis, which makes the surface of the latter uneven, some of its cells protruding over the rest.

4. The mesenchyme is initiated, but does not differentiate. It appears usually as a syncitium with broad cytoplasmic trabeculae. The differentiation of free cells from the syncitium stops, and the differentiation of endo- and ectoplasm (the process by which mesenchyme cells form their basal substance) is also retarded. The latter phenomenon accounts for the great breadth of the cytoplasmic trabeculae in embryos treated with lithium, while in the control embryos only a narrow ring of cytoplasm can be seen encircling the nuclei of their mesenchyme cells.

This retardation in the formation of the basal substance results in the development of cartilage also being retarded. A compact accumulation of crowded cells forms instead of the cartilage rudiments, but these accumulations cannot develop into typical cartilage.

Thus, lithium appears to inhibit quite a number of potencies of the mesenchymal development. The development of the vascular system, however, is an exception to this.

The transformation of mesenchymal syncitium into endothelium goes on in embryos, in spite of treatment with lithium. In vessels formed in this manner primary blood cells develop. Various stages of degeneration may be observed in them, and, probably, these cells die soon after they are formed. Rounded cells of the same kind can be observed outside of the vessels as well, in various parts of the embryo's body, especially in the region of the pronephros tubules. The ap-

pearance of similar rounded cells under deleterious influence was observed by Bauer [9] in the embryos of birds.

5. The state of development of the chorda is different in different embryos. Some of them showed no change even during the later stages. But in a number of the embryos local destruction (swelling) of the chordal tissue could be detected.

When this happens, the chordal tissue sinks into the fissures between the surrounding organ rudiments (myotomes and neural tube). The formation of chordal scars, sunk into muscle segments, was also observed. This phenomenon was observed also in the case of the axolotl [3]. In one of the larvae the muscle segments of the left and right sides were joined through the chordal rupture. In some cases the chordal tissue was pulled into the neurocoel through the fissure in the bottom of the neural tube.

6. At first the muscles begin to develop. Typical myoblastic strings are formed, in which fibrillogenesis sets in. Somewhat later, however, myogenesis stops in the symplastic stage, and real primitive muscle fibres do not form [8].

7. In the entodermal epithelium histological differentiation is entirely inhibited, in spite of active resorption of yolk elements.

8. Three typical pronephros tubules are initiated. Their lumens are greatly expanded, and their epithelia are often in a pronounced stage of degeneration. It is strongly vacuolized, and the apical ends of the cells are decomposed. Nevertheless, when transferred to pure water the cells of the nephritic epithelium regenerate, and the tubules are built up again.

9. Under the epidermis, and sometimes among its layers, cavities are formed which promote bulb swellings, «ventral vesicle» (see above). Such formations were observed also for the axolotl [3].

It is important to note that, in spite of the changes described above, lithium does not interrupt histogenetic processes in some of the organs. Such organs are the suckers, eye cups and crystalline lens, olfactory pit and the auriculary vesicle.

In the last four organs mentioned, full histological differentiation does not yet take place at this stage, but in the suckers differentiation is completed during this stage.

Differentiation of the epithelium in the suckers was found to take place quite normally in the experimental embryos. This is especially noteworthy, since the differentiation of the rest of the epidermal epithelium is greatly inhibited in lithium-treated embryos.

At the same time, it must be noted that a number of organs, although initiated in the experimental embryos, are much behind in development. The organs that behave in this manner are the heart (myofibrilles do not even make their appearance in the myocard), the branchiae, the spine fin and the caudal bud. The regulative processes which take place in the tissues after they have been transferred to pure water will be discussed in another paper.

A comparison of the influence of lithium upon frog embryos with its influence upon the axolotl described in previous papers [3, 4] shows clearly that lithium has some effect common to both cases. On the other hand, a comparison of the influence of various metallic ions (Li, Ca, Mg, K, Na, Zn, Fe) tried in our laboratory on frog embryos shows that the embryo tissues respond quite specifically to the action of various metals. For instance, a comparison of the data given here with those obtained in our laboratory by Vassilieva [10], who studied the influence of calcium upon the histogenetic process in frogs, shows that the only common feature in the effect of Li and Ca is that the ions of both metals retard development. But the type of changes produced in the embryonic tissues is quite different, which gives ground to assert that various chemical factors produce specific changes in morphogenetic processes.

Department of General Biology.
Naval Academy of Medicine.

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